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4 *Men* . . . 4 *Problems*

How to increase production . . . reduce wear on dies and tools without increasing costs.

"OUR production jumped 700% between tool settings." "We make cold pressed nuts. With the steel formerly used, we processed from 4000-8000 lbs. of nuts per day. Last month, using U·S·S Controlled Steel, our records show we processed from 8000-11,000 lbs. per day, about the maximum that can be obtained on our machines. Have about doubled our output.

"On one set of dies we formerly processed 10 to 20 tons of material. We now process 140 tons. 400 to 3000 nuts was the best we could get with one punch—now we get 20,000. Do you wonder we're enthusiastic about U·S·S Controlled Steels?"

How to meet difficult hardness specifications and obtain minimum uniform warpage.

"I'M a gear manufacturer." "We're supplying flywheel gear bands to very close hardness specifications on the tooth and body. Finished dimensional tolerances are within very narrow limits. A carbon steel, to meet these high requirements, must be closely controlled as regards many quality factors. It must readily form, weld, machine and heat treat. Wide variation in the gear sections demands careful selection to ensure the proper combination of quality factors for individual jobs. By using U·S·S Controlled Steels, both coarse and fine grain, we maintain a high excellence in the finished product, have noticeably improved our operation."

How to get rid of trimmer cracks . . . how to minimize scale effect on hardenability.

"WE make connecting rods, cams, front axles and other automotive forgings." "Ease of forging, well-filled sections, and uniformity in heat treatment are advantages that U·S·S Controlled Steels have shown in our plant. Freedom from trimmer cracks and quench cracks, together with marked toughness after heat treating are also imparted by these steels. So is definite uniformity of hardness from center to outside of each product. By using Controlled Steels, and our special agitating equipment, we've minimized the scale effect on hardenability and in addition have achieved a freedom from scale that has materially reduced cleaning costs."

UNITED STATES STEEL

Aluminum in Marine Construction

H. D. McKinnon

Development Engineer,
Aluminum Co. of America,
Pittsburgh, Pa.

Roof of the Gold Star Mother, *Most Recent Ferry Boat Plying between the Battery and Staten Island. More than 65,000 lbs. of aluminum have been used in the construction of this vessel, and a similar amount is being used for the sister ships of this ship, the* Mary Murray *and the* Miss New York, *soon to be put into commission.*

WHEN NEW YORK'S NEWEST FERRYBOAT, the *Gold Star Mother,* slid off the ways with 65,000 lb. of aluminum shapes and plate in her construction, the copious use of the light, silvery metal caused a flutter among marine architects. When it further became known that the two sister ships of this boat, the *Mary Murray* and the *Miss New York,* were to have a similar amount of aluminum on board, there was general cause for wonder.

It is still not universally known that aluminum has a definite place in the marine field, but the eyes of the skeptics may perhaps open a little wider when they hear that the 22 lifeboats of the Holland-America's flagship, the *Nieuw Amsterdam,* are made of aluminum, and that the partition bulkheads in the passenger quarters of the *Normandie* are also of aluminum. The United States Navy uses many pounds of aluminum annually in the construction of bulkheads, pipe berths, furniture, panels, sideboards, and lighting fixtures.

The use of aluminum in marine applications dates back almost to the time when the metal could be made inexpensively enough to become available in quantity. That was subsequent to Charles Martin Hall's discovery of the electrolytic process of reducing aluminum from its ore. Prior to 1886, the date of Hall's discovery, the metal was exceedingly costly, and only a small amount of it was made each year.

When this new metal became generally available, it captured the fancy of the most conservative. It had many excellent qualities, chief among which, at that time, was its lightness. A great future was predicted for it, and the endless talk about such a revolutionary material as aluminum gave rise to a malady which coursed through the veins of almost everyone at the time.

"Aluminum Fever"

Today this malady has been diagnosed as the "aluminum fever." It consisted of an almost rabid enthusiasm. No limit was put to the possibilities of aluminum: Visionaries saw it used for house construction, railroad trains, and many other applications which were actually successful only years later. Because of this aluminum fever, many objects were made of aluminum which had never been made of it before. Marine history has any number of examples.

In 1898, the French Government was disposed to dispute the British sphere of influence on the upper reaches of the Nile, and accordingly dispatched Col. Jean-Baptiste Marchand from the Congo to Fashoda, where he talked the matter over with the great Kitchener.

The journey by the French detachment was made through the jungle. Part of the equipment taken along consisted of an aluminum portable boat, to be used on the Nile if necessary. This boat, built in 1893, was one of the first to be made of aluminum. There were a number of others in those days which had aluminum applications; two French torpedo boats, a naphtha launch, a racing yacht, a German steamer, two Dutch gunboats, a racing shell. F. G. Jackson, a Polar explorer, took an aluminum boat with him to Francis Joseph Land in 1894, and Walter Wellman had some aluminum sled boats in the Arctic in the same

Centerpiece from the Cast Aluminum Ceiling in the Grand Hall of the Nieuw Amsterdam. *Designed by John Raedecker in collaboration with John Polet, the symbolism in the subject expresses the axis of human life: Marriage and Child.*

year. The Illinois Pure Aluminum Co. built 12-ft. hunting boats of aluminum, weighing only 50 lb.

Aluminum in the "Defender"

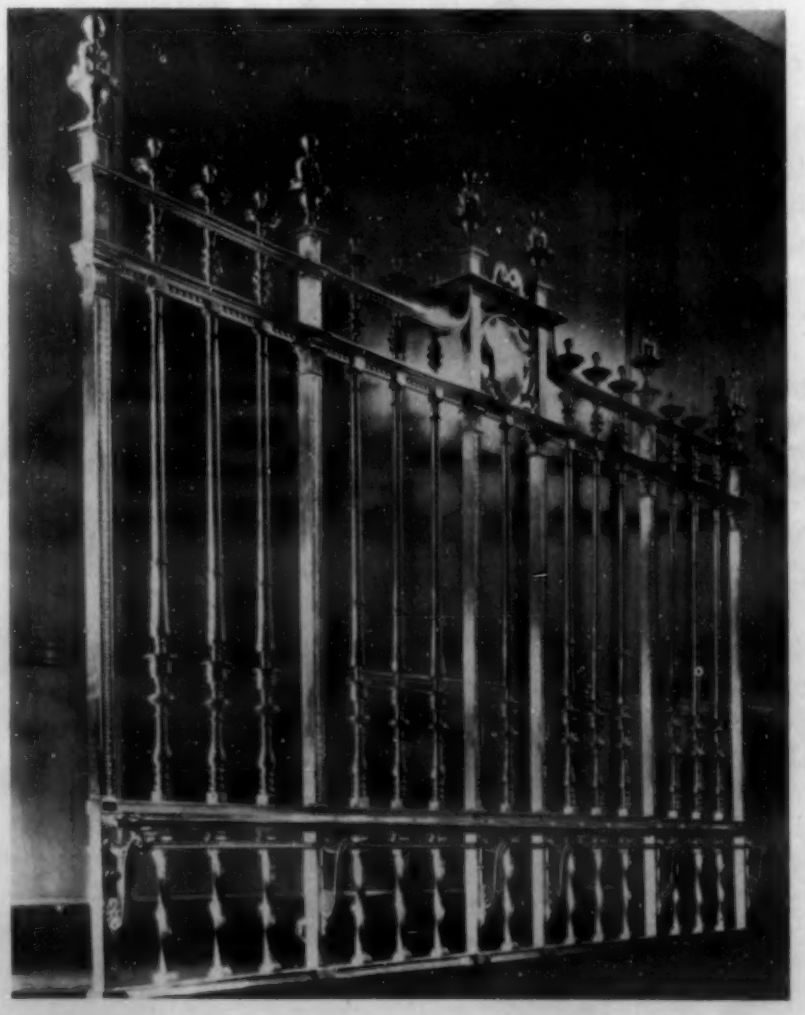
The significant thing about all this activity was that people were convinced that aluminum had a place on the water. This trend of thought was graphically demonstrated in the construction of the *Defender,* the sloop which won the America's Cup races of 1895 when she defeated the British challenger *Valkyrie III.* Winfield M. Thompson and Thomas W. Lawson, who wrote "The Lawson History of the America's Cup" in 1902, give an interesting account of this radical vessel:

> The greatest secrecy was maintained regarding her. Lightness to the last degree consistent with speed was the chief aim in her construction. Expense was not regarded in building her, and in the use of so light and strong a metal as aluminum in her construction Herreshoff realized a dream—though an empty one, it seems—of yacht designers. *Defender* was the second yacht in which this metal was freely used, the first being a French boat called *Vendenesse,* built in 1892. *Defender's* topside plating, which was laid to overlap, her deck beams, her braces under the deck, and stringer plates connecting the deck beams with the side of the vessel, as well as her rails, were aluminum, alloyed with from 10 to 15 per cent of nickel and steel. Her deadlight frames and covers, small interior fittings, and the sheaves of her blocks were also of this metal. Her bottom plates and keel plates were of manganese bronze, of the same weight as Tobin bronze, and her frames, stem post, floor plates, stiffening angles, underdeck beams, two deck beams enclosing the mast, tie-plates around the mast, step-socket, bedplate, fittings and supports, and chain plates were of steel. All her fastenings were of bronze. Her aluminum plates were from 5/16 to 3/8 in. thick, a plate of the former thickness having an ultimate tensile strength of 40,780 lb. per sq. in. This metal was computed to be 2 3/10 times lighter than Tobin bronze, with which *Vigilante* was plated. Naval Constructor Richmond Pearson Hobson, discussing the use of aluminum in the hulls, is the authority for the statement that by its employment in the *Defender* about 17 tons of deadweight was saved.
>
> While the object of extreme lightness, combined with a reasonable degree of strength, was attained in the *Defender* she was never strong enough structurally to make her a safe boat for the give-and-take of ocean racing. She was notably weak in the neighborhood of her mast step, and it was feared before her first season was over her mast might, under severe strain, put a hole through her bottom. Although practically rebuilt in 1899, she lasted less than six years, and was broken up in 1901, at City Island, in Long Island Sound. The cause of her short life was rapid corrosion in her hull, owing to galvanic action induced by the combination of metals employed, and absence of precautions in construction to minimize such action. She was the extreme racing machine of her day, and her construction was justified in her success in retaining the cup.

This rather lengthy quotation not only describes in detail the various aluminum applications on board the *Defender,* but it also gives the reason for the sloop's subsequent poor performance. Those who have criticized the use of aluminum in the marine field have consistently pointed the finger of scorn at the *Defender,* a vessel which was built in the early stages of the development of aluminum, when alloys, with high corrosion-resisting properties, which prevail today, were not yet in existence.

Luckily for aluminum, there were those who would not be discouraged. Year after year they persisted. In 1896 President Grover Cleveland used an aluminum duck boat on his sporting excursions on Buzzards Bay, one of a number made by the firm of W. H. Mullins, of Salem, Ohio. An 18-ft. boat, made of aluminum and weighing 200 lb., was sent to the Klondike in 1898 from Glasgow.

A Recent View of One of the Aluminum Grilles Installed on the Cunard Line's Mauretania *in 1907. This grille was in excellent shape when taken from the ship when she was scrapped in 1935. The new* Mauretania, *now being built, will have aluminum funnels.*



Aluminum in "Shamrock I"

In the following year *Shamrock I* had not only aluminum topsides, but also aluminum spars, including an aluminum topsail yard, and two United States torpedo boats had aluminum conning towers, galleys, hatch covers and cowls. The *Independence,* built by Thomas W. Lawson in 1901 as a possible America's Cup choice, had an aluminum deck.

One of the most striking instances of the use of aluminum on the high seas may be found in the grilles which were installed on the old *Mauretania,* built in 1907. The ship was taken out of commission in 1934, after 27 years of service. The aluminum grilles at that time were in excellent condition. One of them now occupies a place of honor in New York, in the display room of the Aluminum Co. of America, where anyone interested may inspect it. Twenty-seven years of constant exposure to salt air have not left their mark.

In the America's Cup Races

In a dissertation on the use of aluminum in the marine field there is one theme that constantly recurs: The use of the metal in the sloops that contended for the America's Cup. Racing machines they were, pure and simple, and they were built to do only one job, and to do that job well. Theirs was not to be a long life, but a fast and exciting one. Any developments which could add to the performance of these vessels, in one way or another, were eagerly made. Cost was no consideration.

The weight of equipment above deck was always an item which attracted the care and caution of the designers. For every pound of weight saved aloft, a pound could be saved in the keel. The less deadweight such a vessel had to carry, the faster it was apt to be. In recognition of this nautical law, the builders of the *Vanitie,* which was to defend the America's Cup in 1914, equipped it with a jib topsail sprit, two jib topsail poles, and a gaff—all of which were made of aluminum. The race was never held, for the World War broke out just before the race was to start. Sir Thomas Lipton immediately returned to England to give his time to his country, and all activities here in the United States which concerned the race were cancelled.

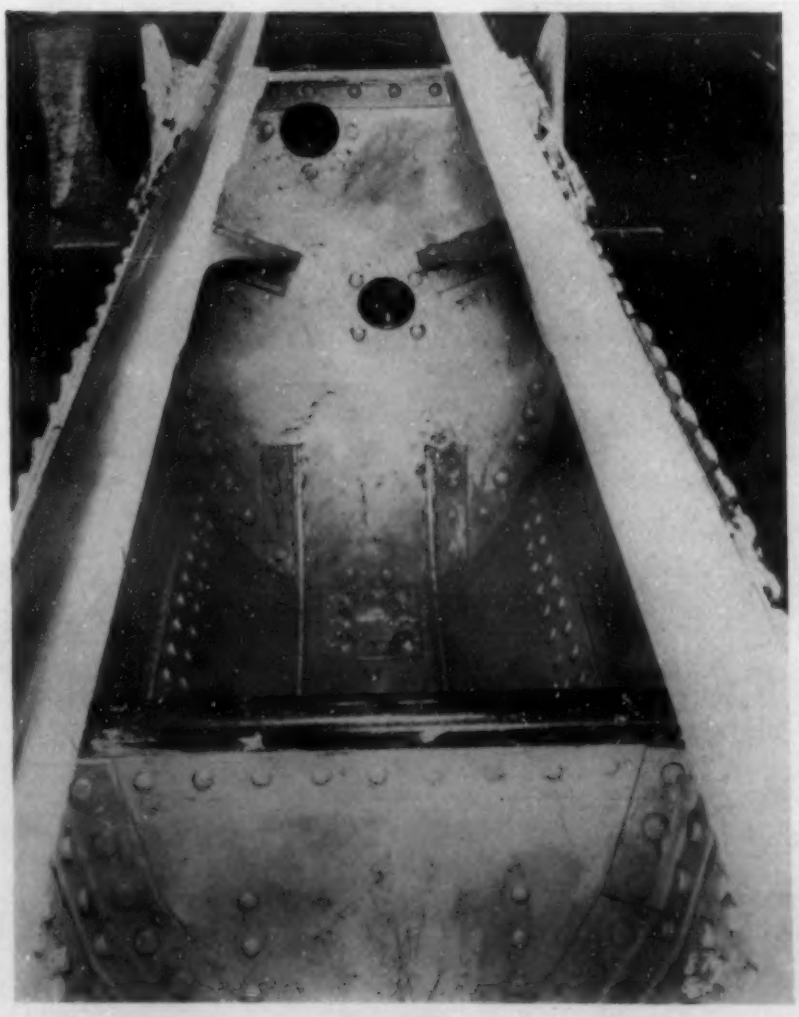
Sir Thomas challenged again in 1920, lost, and sent his fifth challenge to the New York Yacht Club in 1930. The sloop picked to defend the Cup was *Enterprise,* owned by a syndicate headed by Harold S. Vanderbilt. Again the problem of saving weight aloft occupied the attention of W. Starling Burgess, the designer. A 165-ft. wooden mast weighs about three tons—a weight which exerts a tremendous amount of leverage on the racing machine. Hitting upon the idea of using an aluminum mast in place of its wooden prototype, Mr. Burgess cut down the mast weight to 4,200 lb., saving almost a ton of weight aloft. This aluminum mast was dodecahedral in cross section, and the aluminum plates were secured by 80,000 aluminum rivets.

Masts of Aluminum

A rash of aluminum masts made their appearance during and after the 1930 races. *Whirlwind,* eliminated as a Cup defender in the trial races, also had an aluminum mast. In 1931 an aluminum mast was stepped into the all-aluminum pleasure cruiser *Diana II,* and in the next year

Close-Up of Rainbow's *Mast Showing Structural Details*

View of Two of the Traverse Bulkheads Used to Strengthen the Interior of Rainbow's *Mast. Note the riveted construction and fairleads through which lines for the sails are passed. The lines were run up the interior of the mast in order to reduce wind resistance.*



An All-Aluminum Pleasure Cruiser Which has been in Service Since 1931 is the Diana II, *Owned by Donald van den Bergh of England. This vessel is 55 ft. long and is used in Mediterranean waters. It has an aluminum hull, aluminum fittings, aluminum rails, aluminum pilot house, an aluminum dinghy, an aluminum mast and many other applications.*

the masts of a number of British yachts and small racers were made of aluminum.

Yankee's aluminum applications were confined to fittings, *Endeavor I's* to grilles. The Class M sloops *Avatar, Prestige,* and *Valiant* were each equipped for the 1934 racing season with a 100-ft. aluminum mast. In 1935 *Prestige* won 24 races out of 24 starts. Smaller vessels equipped themselves with aluminum mainmasts, mizzen masts, dandy masts, and booms.

The advantages to be gained from building a mast in aluminum are obvious when considering the 1,800 lb. of weight saved by the aluminum mast of *Enterprise.* Not so obvious are the advantages in the case of *Rainbow,* the 1934 defender, and *Ranger,* the finest racing yacht of them all, because of the change in rules regarding mast weights. There were no limitations in mast weights prior to 1934, but in that year the Race Committee heeded the request of T. O. M. Sopwith, *Endeavor's* owner, and decreed that the minimum weight of a Cup yacht mast was to be 5,500 lb. Last year that minimum was increased to 6,170 lb. *Rainbow's* mast weighed 5,685 lb.

As knowledge of streamlining progressed, changes in design were reflected in the masts of Cup yachts. The 1934 masts (*Rainbow's* and *Weetamoe's*) were pear-shaped and thus lessened wind resistance. Because of this streamlining, fewer aluminum plates were needed, and the number of rivets was cut down to 20,000, further reducing wind resistance. Even greater advance in obtaining a smooth mast exterior was made in *Ranger's* elliptical masts, which, by reason of their symmetrical shape and the width and thickness of the plates used, required only 12,000 rivets. These rivets were countersunk, where previous masts had button-head rivets.

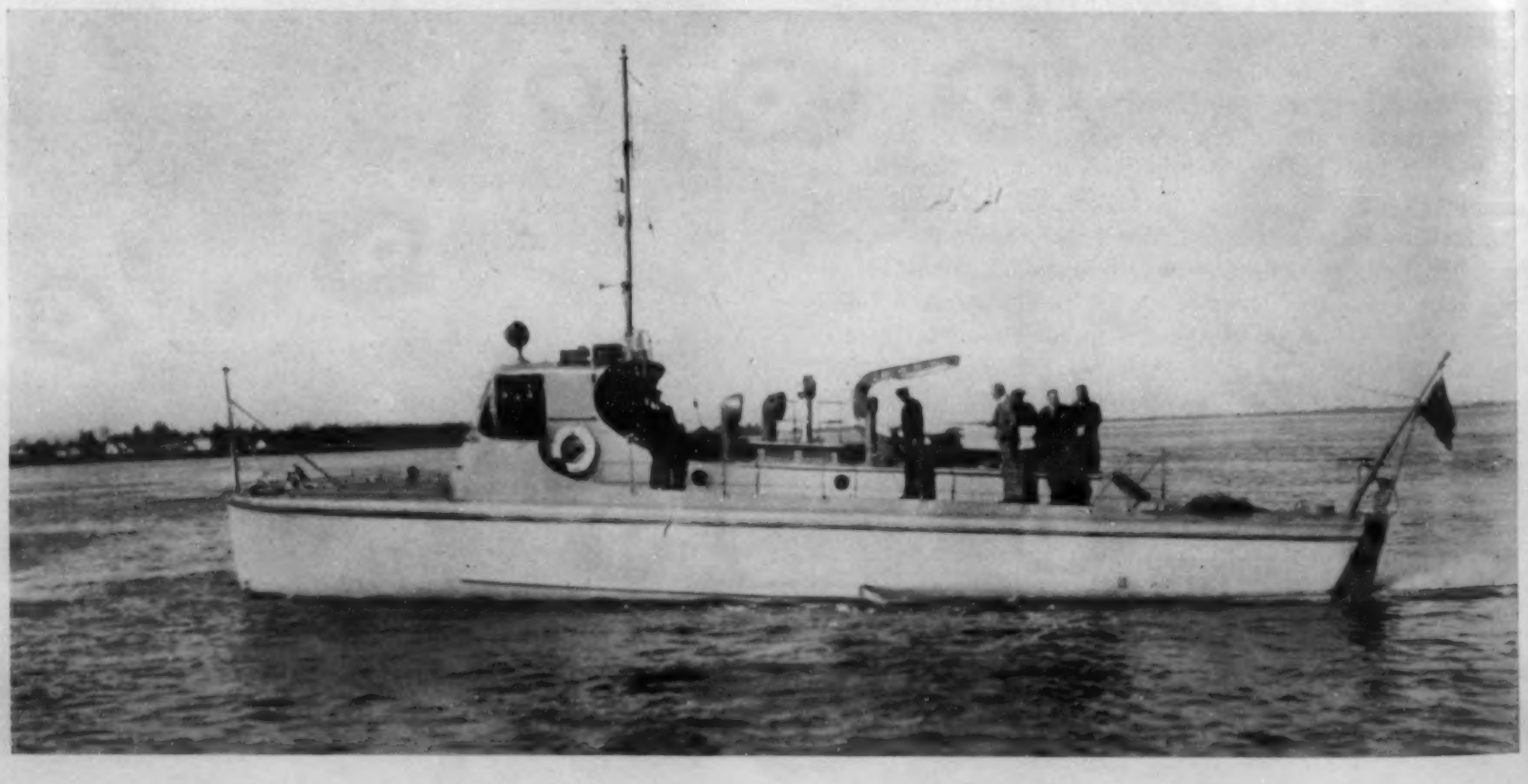
Although the present restrictions on masts for America's Cup yachts require a minimum weight based on the water line length of the vessel, and a center of gravity not lower than 40 per cent of the mast's overall length above the butt, there is still a decided advantage in using aluminum. The shell of a steel mast of the required weight is so thin that it has to be reinforced with closely spaced internal rings to prevent local crumpling, or "secondary failure," as it is called.

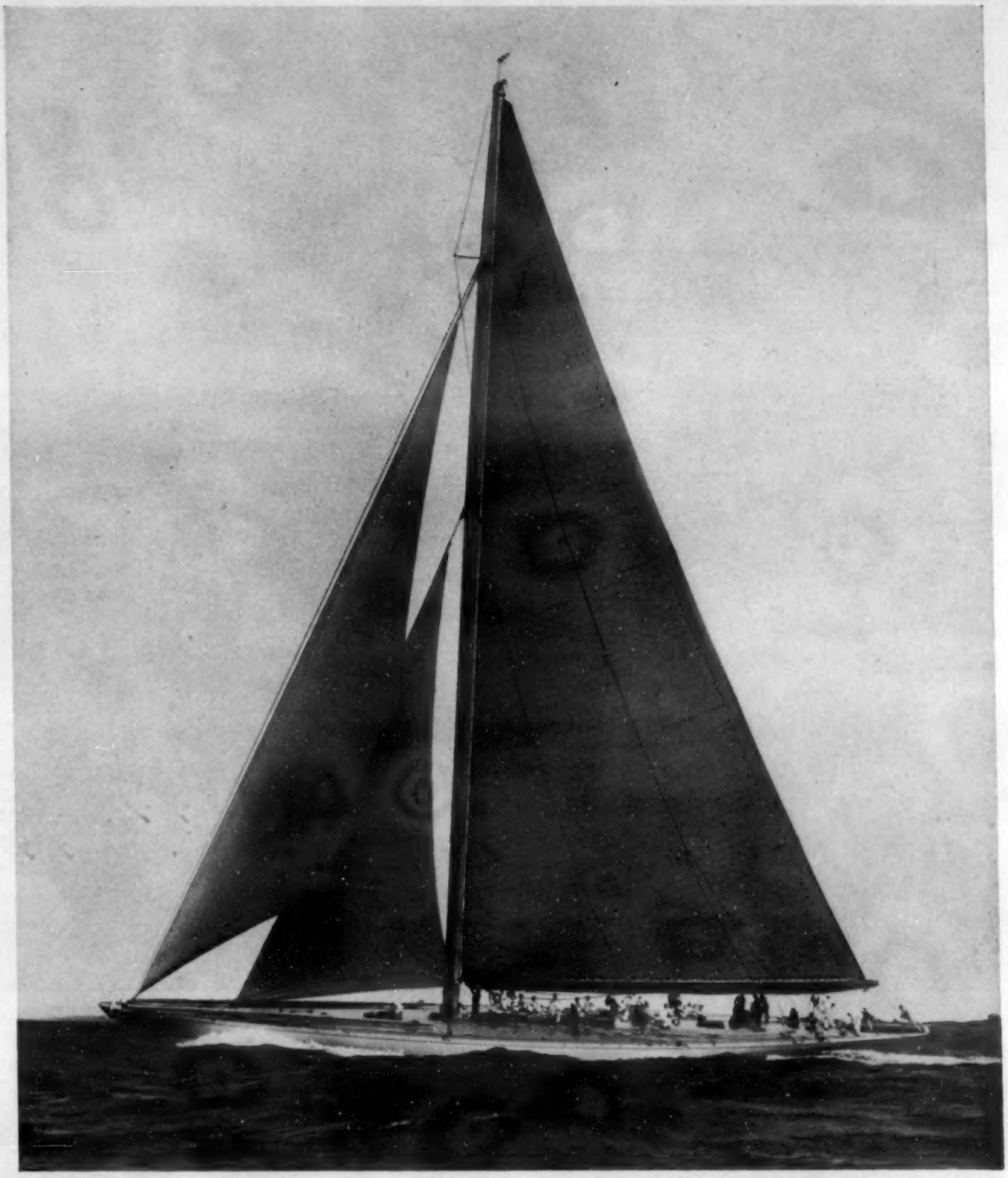
The weight of these reinforcing rings must be subtracted from the weight available for the mast shell, which leaves the steel mast a weaker column than the aluminum mast. Both aluminum and steel are vastly stronger than wood for spars of this size.

Spars and Booms of Aluminum

It is interesting to note that *Ranger* was the first large yacht to have all-aluminum spars. In addition to her aluminum mast she had an aluminum boom and two

The 65-ft. All-Aluminum Patrol Boat Interceptor. *This vessel is used by members of the Royal Canadian Mounted Police to curb the activities of smugglers at the mouth of the St. Lawrence River.*





Ranger *With a Bone in Her Teeth. Her two aluminum masts were built in the shops of the Bath Iron Works, where* Ranger's *hull was also fabricated, and Bath officials, great believers in the future of aluminum on the high seas, agreed to build both boat and mast on a straight commercial basis. Yachtsmen privileged to watch the mast under construction marveled at the beauty of the tall stick, at the workmanship apparent in every joint, and at the confidence with which this well-known shipbuilding firm approached the problem of using a material relatively new to the sea.*

aluminum spinnaker poles. An aluminum boom was purchased for *Rainbow* in 1936, two years after the Cup race she won.

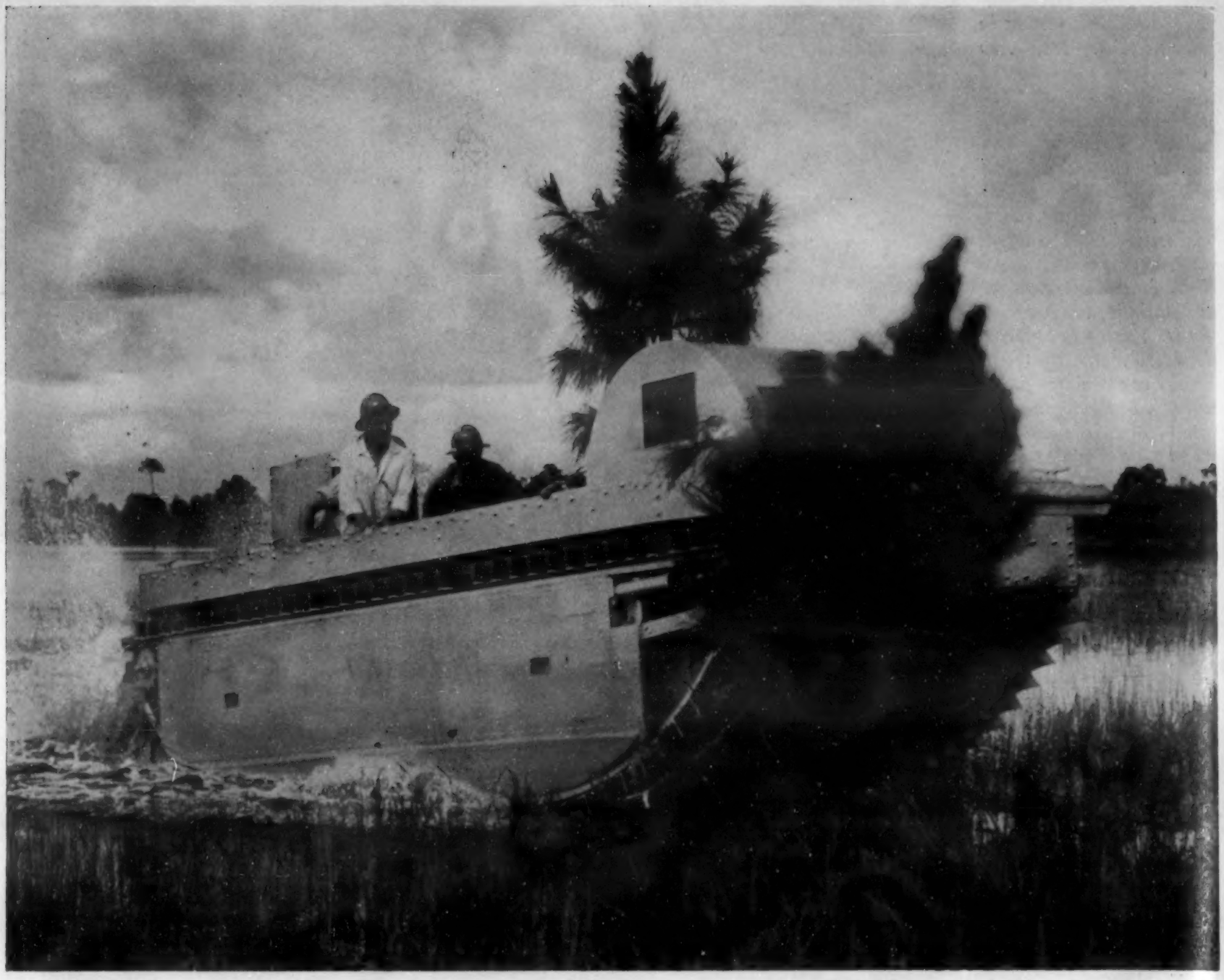
In designing the latest type of aluminum masts for Cup yachts, mechanical limitations of construction required that certain minimum thicknesses of metal be used. This was particularly true where highly concentrated loads were introduced. To obtain a weight comparable to aluminum in heavier structural materials, the sections would have to be one-third as thick as aluminum, for aluminum weighs only a third as much as other common metals.

With aluminum only a seventh of an inch thick at the top of the mast, the use of any other material would complicate matters, and it would be practically impossible to employ many of the new features of the mast truck because the relation of strength to lightness could not be maintained. Building aluminum masts for Cup racers is still a highly specialized field, even though there are now enough of them in service to take them out of the experimental stage. That they are amply strong for their arduous tasks was demonstrated by *Ranger's* first mast, which took such an unmerciful lashing, following the destruction of its standing rigging, before it finally snapped.

Ranger's first mast was so much stronger than it needed to be, that the gage thickness of all plate on the second mast was reduced by 5 per cent.

So much for aluminum masts. A number of ocean-going vessels have been equipped with aluminum dining chairs, and in spite of constant exposure to salt air, these have held up very well. Almost 600 aluminum chairs may be found on each of the Matson Line's three largest ships, the *Mariposa,* the *Monterey,* and the *Lurline.* Aluminum chairs are also part of the equipment on a number of ships belonging to the Waterman Steamship Corp. and to Moore & McCormack.

Another interesting application of aluminum in the marine field is the foil insulation with which hundreds of ships are equipped. This material weighs only one-seventieth as much as the cork it replaces, and has been used in shipbuilding ever since 1926.



A View of the 8,700-lb. All-Aluminum "alligator" Designed and Built by Donald Roebling of Clearwater, Fla. This device can travel on both water and land and will be used for swamp patrol and rescue work.

Vessels All of Aluminum

All-aluminum vessels are relatively recent. *Diana II,* mentioned above, has been in commission since 1931. Her hull, fittings, davits, dinghy, deck, bulkheads, and accessories are aluminum. An all-aluminum tender was built in 1932 for King George V's sloop, *Britannia,* and a similar tender, but smaller, was built a few years later for W. L. Stephenson's *Velsheda.* A 65-foot all-aluminum cutter is the *Interceptor,* which patrols the mouth of the St. Lawrence River in search of smugglers.

Many of the motor boats which compete for the outstanding racing trophies have hulls of aluminum. All outboard motors are made of aluminum because of the metal's lightness.

While the mention of the *Nieuw Amsterdam's* lifeboats in the second paragraph is interesting, it should be noted that these are not the first to be built in aluminum, nor, it is hoped, will they be the last. Two years ago ten lifeboats were built in England for the *Awatea,* a New Zealand ship, and at present there is an aluminum lifeboat in service on the United Fruit Co.'s *Veragua.*

In the period from 1926 to 1934, 50 pontoon boats of aluminum were built for the U. S. Army. All of these are in service today, and their performance record has been such that 12 additional boats were built for a similar purpose last year. These boats are 26 ft. 6 in. long, have a 5-ft. beam at the gunwale, and are 2 ft. 7½ in. deep at the center section. Each weighs 1,200 lb., 750 of which are aluminum. Each carries a crew of 5 and 25 fully equipped riflemen. The maximum safe load of the boats, when used as pontoons, is 16,000 lb. gross load per bay, with maximum single axle load of 10,000 lb. The distance between axles is 9 ft. A bridge made of these pontoon boats can carry light tanks, three-ton trucks loaded, or five-ton trucks with a load not greater than two tons.

Airplanes of Aluminum

It need hardly be mentioned, in a treatise such as this, that most airplanes used today are made of aluminum, and that their hulls and pontoons, if they are hydroplanes, are made of a special alloy of aluminum which has exceptionally good corrosion-resisting qualities. It is interesting, however, to note how the applications of aluminum have gripped the imagination of many mariners. Even iceboat enthusiasts are now beginning to equip their craft with aluminum fittings. *Trudel III* and *Swordfish,* well known on the icy reaches of New Jersey lakes, owe some of their records to the aluminum masts they carry.

Gases for Controlled Atmospheres

—REQUIREMENTS FOR PURIFICATION

by E. E. Slowter and B. W. Gonser

Chemical Engineer and Metallurgist, Respectively, Battelle Memorial Institute, Columbus, O.

This article is another in an array of important contributions to the general subject of controlled atmospheres which have been published from time to time by METALS AND ALLOYS. In the preparation of gases for use as controlled atmospheres in heat treating many steels, purification or an adjustment of composition has been found necessary to meet certain conditions such as bright annealing, hardening without decarburization, and so on. To accomplish certain desired ends, the purity and composition of the atmosphere must be controlled. This discussion covers some of the problems and their solution. It has a strong appeal to all steel treaters.—The Editors.

EARLY ATTEMPTS TO PREVENT surface changes in steel during heat treatment, due to reaction with the surrounding atmosphere, consisted essentially of avoiding as much as possible the presence of free oxygen. The convenient method of passing the products of combustion of the fuel used over the steel, for example, did help keep oxygen away from the work but left much to be desired in the way of controlling the reactions since the flue gas was itself oxidizing.

Some measure of control was obtained with the advent of gas generators which could produce a cheap, oxygen-free atmosphere of composition controllable within certain limits by partial combustion of fuel gas, or by passing air through hot carbon. The gas from such generators, however, was found to be by no means fool-proof. Some constituents of the gas, (water vapor and CO_2) could readily oxidize the steel; H_2 was usually an active decarburizer; CH_4 and CO could carburize low-carbon steels; and to make matters worse, combinations of these components added complexity to the reversible reactions which were already influenced by conditions of time, temperature, concentration of components and type of steel present. To make the gas usable for heat treating many steels, therefore, it has been found necessary to purify or adjust the composition of the gas originally produced.

Removal of water vapor has been recognized for some time as an essential step in making generator gas less reactive. Since CO_2 can readily react with H_2 to form more water vapor, this step has been of little or no help in some treatments, as in preventing decarburization of medium and high carbon steels when heated over about 1500 deg. F.

The tendency recently, then, has been to eliminate the CO_2. Complete elimination with commercial apparatus is difficult, hence there has been need for information on the effect of residual CO_2 in the gas and on the extent to which it must be removed when treating various steels. Likewise, information has been needed on the possibilities of counteracting residual CO_2 with small amounts of CH_4. It has been shown in previous work that the addition of a little natural gas, i.e. CH_4 or its equivalent, is beneficial under many conditions in counteracting decarburization.

The purpose of this discussion is to give information on the effect on various carbon steels of small amounts of CO_2 and of CH_4 in dried generator gases from which most of the CO_2 has been removed. This includes gases representing the atmospheres produced by dry charcoal producers as well as the more common partially burned fuel gas generators. The experimental work on which this article is based is a further phase of the investigation sponsored at Battelle Memorial Institute by Utilities Coordinated Research, Inc., on gases for controlled atmospheres suitable for use in the heat treatment of steel.[1, 2]

SOURCES OF CONTROLLED ATMOSPHERES

THE GASES used for controlled atmospheres in bright annealing and in hardening without decarburization can be considered as based on H_2 or on CO as the primary protective gases, with N_2 as a diluent. By reviewing the commercial sources of such gases it is evident that the cheaper sources do not give a pure gas, but rather a mixture of gases. Some of these, if harmful, should be removed.

Hydrogen-Nitrogen Gases

The purest such gas commercially available is cracked anhydrous ammonia. By merely heating, the NH_3 is broken down to give 75 per cent H_2 and 25 per cent N_2. Such gas, if truly dry, will serve for bright annealing of stainless steel. Even traces of free O_2 such as are found

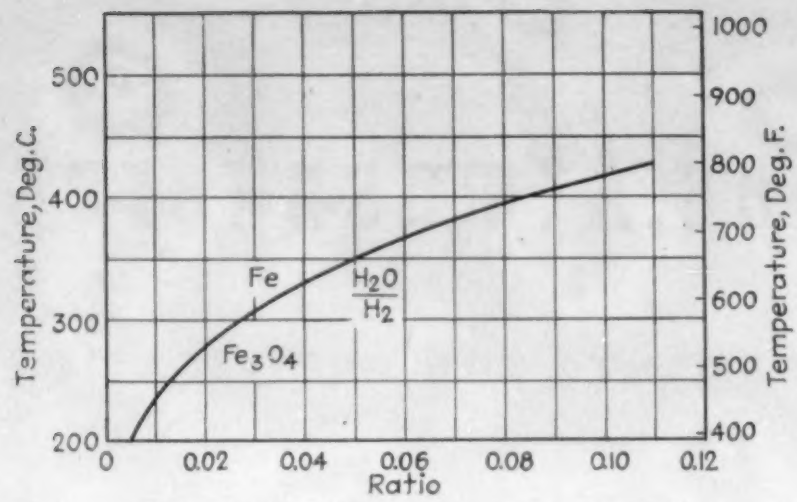


Fig. 1.—Effect of the H_2O/H_2 Ratio on the Oxidation of Iron. (Curve plotted from data given by H. Schenck in "Physikalische Chemie der Eisenhuttenprozesse")

in cylinder H_2, of moisture, or of CO_2 or CO will oxidize high-chromium steels. Indeed the freedom of H_2 and H_2-N_2 mixtures from O_2 in any form is most sensitively tested by passing the gas over hot stainless steel. A more dilute H_2 may be obtained by burning this 75 per cent H_2, 25 per cent N_2 gas with a deficiency of air and removing the H_2O formed. The N_2 of the air dilutes the gas and makes a somewhat cheaper mixture.

Hydrogen-Carbon Monoxide-Nitrogen Gases

Methane or other hydrocarbon gases can be cracked in the presence of a little air and some steam to produce mixtures high in H_2 and CO which are useful in "hydrogen" brazing. By adding more steam over a nickel catalyst, the CO may be oxidized to CO_2, the CO_2 removed by absorption with NaOH or similar absorbent, and the gas then dried. Various mixtures can be thus produced, varying from those high in H_2 (35 per cent or even higher, and 20 per cent CO with small amounts of CO_2, H_2O and CH_4) down to one of 5 to 10 per cent H_2, 90 to 95 per cent N_2. The 5 to 10 per cent H_2 gas has been used as a commercial protective atmosphere, but the cost of the generating and purifying plant is so high that only in a very large installation is such a method cheaper than the use of partly burnt, cracked NH_3.

By burning a fuel gas with only a very slight deficiency of air, but taking care to get all the free O_2 of the air into combination, a flue gas high in CO_2 and low in CO, H_2 and CH_4 is obtained. Starting with natural gas, one could produce a gas of about 10 per cent CO_2, 2.5 per cent CO, 1 per cent H_2, 0.4 per cent CH_4 plus water vapor, from which the CO_2 and water vapor could be removed to give a gas of about 95.6 per cent N_2, 2.8 per cent CO, 1.1 per cent H_2 and 0.5 per cent CH_4. Equipment for making a high-nitrogen gas of this type is understood to be under commercial development. Propane or other hydrocarbon gas could be similarly processed to make rather similar gases of low, but somewhat different, contents of CO, H_2 and CH_4.

Hydrogen-Methane Gases

Cracked hydrocarbons such as natural gas, propane, butane, or oil vapor can be allowed to deposit soot and the resulting H_2, CH_4 gas may be used as a protective atmosphere. The CH_4 content is usually such as to make the gas strongly carburizing; indeed, the heating process becomes one of gas carburizing. The lower temperature in bright annealing and the shorter time in clean hardening, compared to the usual conditions of gas carburizing, decrease the depth of carburization actually attained. Soot deposition on the work may be sufficient to interfere with the finish of the annealed work or to hamper hardening on quenching.

Carbon Monoxide-Nitrogen Gases

In seeking to produce a gas consisting primarily of CO and free from H_2, one may utilize a "dry gas producer" in which dry air is passed over hot, dry charcoal, electrode carbon, graphite, or other pure carbon. This may be termed a "charcoal producer." With sufficient contact of the air and the carbon, and at a sufficiently high temperature, a gas of 33 or 34 per cent CO, 0.25 per cent CO_2, balance N_2 can theoretically be made. In practice, a gas of 28 per cent CO, 3 per cent CO_2 is more likely to be made, and if moisture is present, this will react with carbon to give CO and H_2, together with a little CH_4 so that from 1 to 4 per cent H_2 may also be present. The ordinary gas so made will thus carry, say, 29 per cent CO, 3 per cent CO_2, 2 per cent H_2, 0.5 per cent CH_4.

Partly Burned Fuel Gases

The gas that is cheapest and most easily available for controlled atmosphere work is made by burning a fuel gas with a deficiency of air and cooling the product gas with water sprays or cooling coils so as to remove all the water except that amount with which the gas is saturated at the temperature to which it is cooled. Various factors influence the composition of the gas produced, such as the type of fuel gas used, the gas:air ratio, the temperature of combustion, and the catalyst present. A characteristic generator gas produced from natural gas, as an example, contains about 10 per cent H_2, 10 per cent CO, 6 per cent CO_2, 0.5 to 1 per cent CH_4, 1 per cent H_2O (if chilled to 45 deg. F.) and balance N_2. By burning in the furnace without removal of H_2O, 10 to 20 per cent of steam will accompany these gases. By dehydration over activated alumina, on the other hand, all but a minute trace of H_2O can be removed.

Use of this generator gas for bright annealing low carbon steel at about 1250 deg. F. is well advanced and widespread. When applied to the task of hardening medium and high-carbon steels without decarburization, however, a number of difficulties are encountered and modification of the above composition becomes necessary as described later in greater detail.

In bright annealing at 1250 deg. F. with ordinary generator gas the chief considerations are elimination of all free O_2 and holding the water vapor content to a low value. The presence of CO_2 at this temperature is not such a factor as it is when hardening higher-carbon steels at higher temperatures, since the usual CO_2:CO ratio (as 0.6) does not produce scale. The trouble with free O_2 usually can be satisfactorily overcome at the source by proper burner adjustment, using refrigerator coils to eliminate O_2 picked up from water sprays and by stopping air leaks into the furnace. If necessary, the inlet gas may be led over hot steel chips to consume free O_2 before the gas enters the furnace.

Water vapor normally causes no harm at the bright an-

nealing temperature, in fact, a small amount is desirable to maintain equilibrium conditions and prevent etching,[3] but as the temperature drops (in cooling the charge) oxidation or staining will occur if the H_2O:H_2 ratio exceeds a definite limit. This is shown in Fig. 1. At 800 deg. F., for example, a ratio of over 0.1 (1 per cent H_2O:10 per cent H_2) will cause oxidation but, if the charge can be quickly cooled through the temperature range where the ratio is likely to be exceeded, there is little danger of staining. The presence of CO_2 complicates the situation since the following water gas reactions are catalyzed by contact with steel.

$$(1)\ H_2 + CO_2 \rightarrow CO + H_2O$$
$$(2)\ CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O$$

Water vapor formed in the furnace by these reactions must be added to that already present in calculating the true H_2O content. This is important in hardening steel where the temperature is sufficiently high for these reactions to proceed rapidly but is of little importance in low temperature annealing.

Due to interaction of the constituents of generator gas in a steel heat-treating furnace, it is of the utmost importance to determine the composition of the exit gas as well as the entrance gas in order to interpret results. The determination of H_2, CH_4 and of water vapor should not be omitted. Frequently, in commercial work, such as in controlling a bright annealing furnace, moisture is omitted from the determination. This is inexcusable since simple dew point methods, which have been discussed by Stack[4], Hotchkiss[5] and others, are available by which the moisture content can be readily determined. A jump in H_2O in the exit gas would indicate that some change in operating conditions had occurred. These probably could be remedied before conditions got so bad that the work would be stained.

In addition to water vapor and CO_2 which are undesirable constituents of gas from fuel gas generators, sulphur, either as H_2S or SO_2 or a mixture of the two, must be eliminated from the atmosphere, not only to protect the work but also to protect heat-resistant alloy parts and resistor elements. Where possible, fuels very low in sulphur should be selected since removal of small amounts of H_2S is difficult. Available methods for sulphur removal are well covered in the technical literature.

HARDENING WITHOUT DECARBURIZATION

HARDENING medium and high-carbon steels is done at temperatures where inter-gas reactions can take place which create a relatively complex situation when using partially burned generator gas. Fortunately, it is usually not essential to avoid mere staining of the surface, but decarburization must be avoided. Both carbon and alloy steels are concerned in an investigation of this field. They cover a range in carbon content from about 0.15 per cent for a highly alloyed steel to perhaps 1.10 per cent in a carbon tool steel.

Review of Previous Work[1, 2],

The action of protecting gases varies with the carbon content of the steel. Even the decarburization of most representative alloy steels has been shown to be dependent upon the carbon content and not to any large extent on the other constituents. In much of the previous experimental work the effect of various gases on steel samples was studied by heating the samples for 3 hrs. at 1740 deg. F. in order to accentuate tendencies toward carburization and decarburization over those common in practice. Weight changes of over 0.00010 gms. per sq. cm. of surface (10 units on the scale used in plotting results) were required to produce any visible change in carbon content by examination with the microscope or to allow detection of any change in surface hardness. From a practical standpoint it is probable that, at operating times and temperatures, no change could be detected with a 20 unit gain or loss in weight under these test conditions. A loss of 50 units doubtless corresponds to a degree of decarburization under ordinary heat-treating conditions that would be too detrimental to be endured.

The allowable degree of decarburization that may be permitted for the shorter times and lower temperatures of practice, will vary with the requirements imposed on the heat-treated piece, so one user might consider a gas which causes a loss of 50 units in these tests as satisfactory for practical use, while another might demand a gas that would not produce more than 20 units. For many purposes carburization corresponding to 50 units would not be harmful. However, in the case of a very prolonged treatment of a large die block the user might demand that the gas be so nearly neutral to the particular steel as to show not more than a gain or loss of 5 units in this test.

Tests described in the previous publications [1, 2] showed that even dry 75 H_2-25 N_2 from cracked ammonia was decarburizing to all but very low-carbon steels. For example, under test conditions a 0.60 per cent C steel lost 100 units. Diluting with N_2 to give a dry gas containing only 10 per cent H_2 decreased this loss to some 40 units. Addition of about a per cent of CH_4, or even less, satisfactorily overcame this decarburization. Unless the gas was dry, however, severe decarburization occurred which could not be satisfactorily compensated for by addition of CH_4.

The effect of pure, dry, CO-N_2 gases, ranging from 34 per cent to 5 per cent CO was also studied. Although mildly carburizing to very low-carbon steels, none of these gases were appreciably carburizing or decarburizing to steels that would be hardened. Here, too, the presence of moisture was found to be fatal, producing strong decarburization which could not be satisfactorily corrected by CH_4 additions. Moisture, therefore, must be excluded from such a gas.

Studies of the effect of CO_2 in the presence of CO, but without H_2 or H_2O, showed a CO_2:CO ratio as low as 0.1 to produce too much decarburization. With H_2 also present but CO_2 and H_2O absent (pure CO-H_2-N_2 gases), the decarburizing action of H_2 was accentuated over that of a pure H_2-N_2 gas of equal H_2 concentration, but this could be corrected by addition of CH_4. Gas from a dry gas producer was decarburizing unless the CO_2 was removed.

Need for CO_2 Removal

Ordinary undried generator gas is known to be badly decarburizing under steel hardening conditions. Removing the moisture helps at relatively low temperatures, e.g. 1470 deg. F. but some decarburization has been shown[2] to remain, and at higher temperatures, e.g. 1650 deg. F.

sufficient moisture is formed by reaction of H_2 with CO_2 to make the gas as decarburizing as though it had not been previously freed from moisture. By removing CO_2 as well as H_2O, however, a CO-H_2-N_2 gas remains which previous work has shown to be suitable for use in hardening since its tendency to decarburize can be overcome by addition of CH_4. This condition is being recognized and most of the manufacturers of generators for controlled atmospheres are developing equipment for removal of CO_2.

Since CO_2 removal is rather costly, other methods of producing gas for steel hardening atmospheres may be considered. Thus, the amount of CO_2 in a dry (charcoal) producer gas is only about 3 per cent compared to perhaps 6 per cent from a partially burned fuel gas generator, hence the lesser cost of CO_2 removal for the dry producer gas helps compensate for its initially higher cost. Moreover, the dry gas producer gives a product that is higher in CO than that from a fuel gas generator. This permits the presence of more residual CO_2 (i.e. less complete removal) without exceeding a limiting CO_2:CO ratio.

Although it is possible to remove CO_2 completely from a gas, chemical engineers familiar with this operation know that it is not an easy task to remove the last few tenths of a per cent with either caustic or ethanolamine absorbents. The use of gaseous NH_3 for the removal of small amounts of CO_2 left after scrubbing with such absorbents is an interesting possibility but represents an increased investment and maintenance charge. From a practical viewpoint, therefore, it would be a big advantage if the final gas of about a half per cent of CO_2 could be tolerated rather than that the gas be scrubbed entirely free of this unwanted constituent.

EXPERIMENTAL WORK WITH ATMOSPHERES CONTAINING SMALL AMOUNTS OF CO_2 AND CH_4

IN VIEW of the desirability of not having to remove all the CO_2, it is fundamental in working out controlled atmospheres for hardening without decarburization to know the tolerance of the gas for CO_2 and whether corrective additions of CH_4 or other hydrocarbon can be satisfactorily made. An experimental study of these points has been made, using the methods described in the previous publications.

Charcoal Producer Gas

If the air and charcoal or other form of carbon are dry and the CO_2 is reduced to 0.5 per cent, the gas from a dry gas generator will contain about 32 per cent CO and 0.5 per cent CO_2. If the materials are not dry, some H_2 will be present and 32 per cent CO, 2.5 per cent H_2, 0.5 per cent CO_2 may be taken as representative of such a gas. Representing the action of synthetic mixtures corresponding to these atmospheres, curves A and B respectively of Fig. 2 show that a little too much decarburization of the high carbon steels still persist at this CO_2 content in the absence of CH_4. If 1 per cent CH_4 is added, or is present in the gas by reaction of H_2 (liberated from moisture) with carbon, the tendency toward decarburization is checked, as shown in curve C of the same figure. Thus, even the high-carbon steels are not decarburized beyond the 10-unit limit that cannot be detected microscopically.

From these results it may be concluded that the product of the dry gas producer, after being scrubbed to 0.5 per cent or less CO_2 and then dried to eliminate any moisture taken up in scrubbing, should be satisfactory for hardening high carbon steels without decarburization, provided a small amount of CH_4 is present by reaction or addition.

Partly Burned Fuel Gases

Starting with a dried gas of the type which has been previously designated as a characteristic generator gas, a series of tests was made with the CO_2 content of the inlet gas ranging from 5.3 per cent (no removal) to 0.0 (complete removal). Carburization and decarburization in all cases were measured by weight changes of the specimens. Micro examinations have shown these weight changes to agree closely with the degree of change in the steel. In these tests using this generator gas the steel samples were usually stained during the 3 hr. treatment, probably due to a trace of residual O_2.

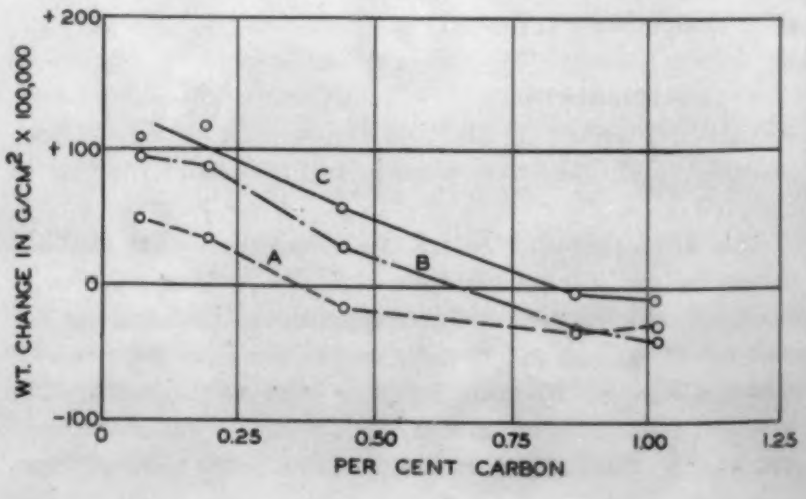
Curve A of Fig. 3 shows the very active decarburization caused by such a gas on high-carbon steels when no CO_2 is removed. Curves B, C, D, E and F of Fig. 3 illustrate the action of this characteristic generator gas when carrying 1.4 per cent, 0.9 per cent, 0.5 per cent, 0.2 per cent and 0.0 per cent CO_2 respectively, representing varying degrees of scrubbing. The CH_4 content was approximately 0.5 per cent in all of these runs though a little variation was caused by the fluctuations in the generator product gas. In making comparisons with data previously reported[1], this CH_4 content should be used although a rounded figure of 1 per cent was used in connection with work on the effect of dry, CO_2-free generator gas on alloy steels.

The CH_4 content should be especially noted in comparing any of the runs of this group since in the range of 0.2 per cent to at least 1.5 per cent CO_2 the amount of CH_4 in the atmosphere is extremely critical. By comparing curves D and E of Fig. 3 the effects of 0.6 and 0.4 CH_4 in an inlet generator gas containing 0.5 and 0.2 per cent CO_2 re-

Fig. 2.—Effect of Synthetic "Dry Generator" Gases on Plain Carbon Steels.

Curve	Atmosphere Composition, Per Cent			
	CO_2	CO	CH_4	H_2
A	0.5	32.0	..	..
B	0.5	35.0	..	2.5
C	0.5	36.0	1.0	2.5

Treatment: 1742 deg. F. (950° C.) for 3 hrs.



spectively, may be compared. However, as soon as the CO_2 is removed down to the equilibrium point, variations in CH_4 have very little effect. A comparison of curves A and B, Fig. 4, shows only a slight increase in carburizing action by raising the inlet CH_4 from 0.4 per cent to 1.1 per cent in such a gas. Carrying this reasoning a step further, as soon as the CO_2 is completely removed, increasing the CH_4 content has practically no effect, as can be seen by comparing Curves A and B of Fig. 5. This would be expected, of course, since as soon as the equilibrium amount of CH_4 is present in an atmosphere, the rate of carburization depends primarily upon the rate of diffusion of carbon into

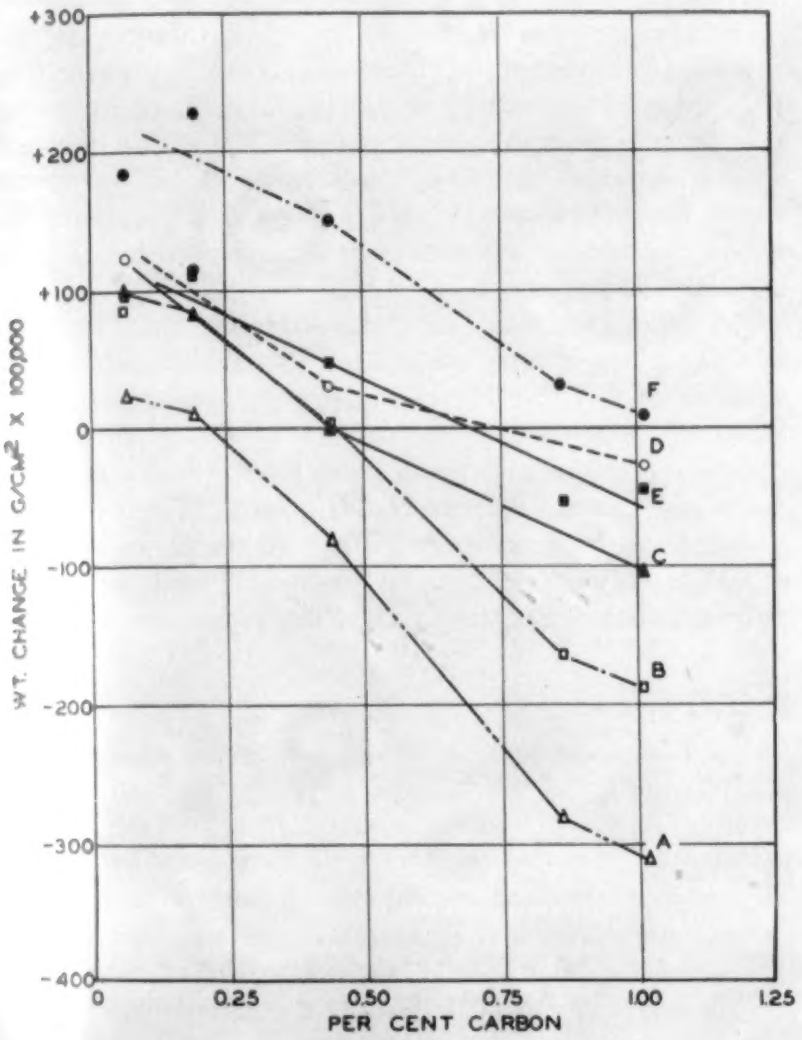


Fig. 3.—Action on Plain Carbon Steels of Dried Partly Burned Fuel Gas Atmospheres Containing Varying Quantities of CO_2 and CH_4.

Curve	Gas Sample	Atmosphere Composition, Per Cent CO_2	CO	CH_4	H_2
A	Inlet	5.3	9.5	0.5	8.8
	Outlet	3.1	13.2	0.5	8.8
B	Inlet	1.4	10.0	0.5	8.5
	Outlet	0.3	11.0	0.5	8.5
C	Inlet	0.9	10.5	0.8	9.6
	Outlet	0.4	10.8	0.6	10.1
D	Inlet	0.5	10.4	0.6	10.1
	Outlet	0.2	10.8	0.7	10.5
E	Inlet	0.2	9.6	0.4	9.3
	Outlet		Same as Inlet		
F	Inlet	0.0	9.5	0.7	9.0
	Outlet		Same as Inlet		

Treatment: 1742 deg. F. (950° C.) for 3 hrs.

the steels and is practically independent of further increases in CH_4.

In considering this equilibrium it is particularly interesting to note in Curves B, C, and D of Fig. 3 that whether the inlet gas contained 1, 0.9, or 0.5 per cent CO_2, the outlet gas contained about 0.2-0.4 per cent CO_2. That is, under these conditions, the gases appeared to approach an

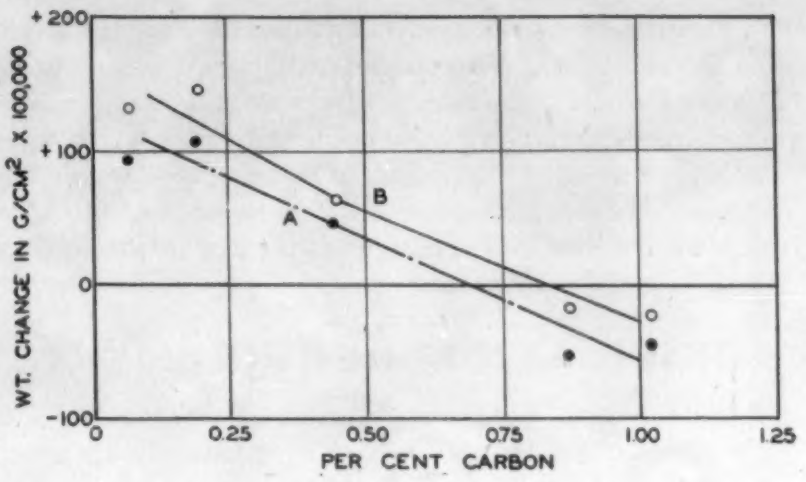


Fig. 4.—Effect on Plain Carbon Steels of Increasing CH_4 Content of a Dried, Partly Burned Fuel Gas Containing 0.2% CO_2.

Curve	Gas Sample	Atmosphere Composition, Per Cent CO_2	CO	CH_4	H_2
A	Inlet	0.2	9.6	0.4	9.3
	Outlet		Same as Inlet		
B	Inlet	0.2	9.5	1.1	8.8
	Outlet	0.15	9.6	0.9	9.5

Treatment: 1742 deg. F. (950° C.) for 3 hrs.

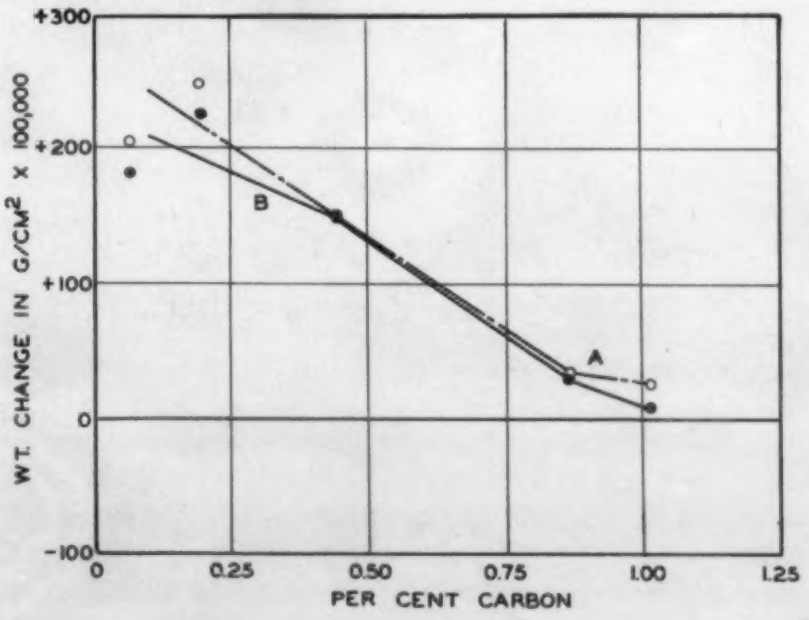
equilibrium at about 0.2 per cent CO_2. To verify this, the inlet gas was made to contain 0.2 per cent CO_2 with the results shown in Curve E of Fig. 3 and Curve A of Fig. 4. It is apparent that under these conditions the gases were in equilibrium, for the inlet and outlet gases were practically identical in composition. The atmosphere itself was as decarburizing as would be expected on the basis of its CO_2 and CH_4 contents. When the amount of CH_4 was increased, as shown in Curve B of Fig. 4, the equilibrium was displaced only slightly and the gas was slightly more carburizing.

These results all appear to be consistent within the limitations previously described for this type of test. The position of the steel in the furnace is a factor of importance

Fig. 5.—Action on Plain Carbon Steels of Dried, CO_2-Free, Partly Burned Fuel Gas Atmospheres with Varying Quantities of CH_4.

Curve	Atmosphere Composition, Per Cent CO_2	CO	CH_4	H_2
A	0.0	9.5	3.5	8.5
B	0.0	9.5	0.7	9.0

Treatment: 1742 deg. F. (950° C.) for 3 hrs.



when dealing with a gas not in equilibrium since the action may differ as the gas composition changes. Soot may be deposited at the entry end of a furnace, for example, and decarburization may be greater at the exit end if water vapor has been formed by reaction of CO_2 with H_2 or with CH_4. In these tests, the same positions were maintained throughout, with the lowest-carbon steels at the end of the furnace which first received the gas.

PURIFICATION REQUIREMENTS

FIRST OF ALL, for any work where decarburization is to be avoided, the atmosphere must be thoroughly dry when admitted to the furnace. In addition, the reactive gases (H_2 and CO_2) in the atmosphere must be so controlled that only such small amounts of water are formed by their reaction in the furnace as can be successfully neutralized by the carburizing components of the atmosphere (CH_4 and CO).

Because of these requirements a knowledge of the H_2, CH_4 and H_2O content of any controlled atmosphere is necessary to understand its action, especially in view of the extreme potency of the CH_4 and H_2O. The determination of H_2O has already been discussed but the determination of H_2 and CH_4 needs further emphasis. Too often controlled atmospheres are condemned because the results obtained are erratic even though routine Orsat analyses show a constant gas composition. The true trouble, of course, lies in a change in one or more of these components which are neglected in an Orsat analysis. Frequently both the H_2 and CH_4 are observed to change greatly in a partly burned fuel gas without much corresponding change in CO. The remedy is to analyze for the H_2 and CH_4 by some suitable method.

Atmospheres of partly burned fuel gases and from dry gas producers are most easily controlled and more nearly universally applicable when the CO_2 is completely eliminated. However, they may be used for non-decarburizing hardening if the CO_2 can be reduced to the equilibrium value and sufficient CH_4 added to make the atmosphere non-decarburizing to the high-carbon steels. Since this equilibrium value depends upon the carbon content of the steel, the temperature of use, catalytic effects of the work and furnace surfaces, time of contact, etc., no definite universal values can be given. With the high temperatures used in this work it seems likely that if the CO_2 content of partly burned fuel gases is reduced to about 0.2 per cent and that of dry producer gases to about 0.5 per cent, non-decarburizing hardening can be obtained by addition of small amounts of CH_4. Other factors being equal, a dry producer gas can stand more CO_2 than a partly burned fuel gas because of the higher CO content of the former. Addition of CH_4 in amounts greater than 1.0 to 1.5 per cent is not practical at higher temperatures because of soot deposition; in fact, no more should be added than is essential to prevent decarburization.

As a rough rule it may be said that in most dry atmospheres, containing no more than a residual amount of CO_2 (0.2-0.5 per cent), an amount of CH_4 equal in per cent by volume to the weight per cent of the carbon in the steel is sufficient to prevent decarburization in any given case. Because of soot deposition, higher hydrocarbons are not as suitable for preventing decarburization, but may be used in certain cases.

An atmosphere, containing H_2, or H_2 and small amounts of CO_2, which is made neutral to high-carbon steels by the addition of CH_4 will be carburizing to low-carbon steels. However, a partly burned fuel gas of this type is more carburizing to the low-carbon steels than a similar dry producer gas. Relatively pure H_2-N_2 gases need only be compensated for the decarburizing action of the H_2 by addition of CH_4. In this case, also, an atmosphere neutral to high-carbon steels will be carburizing to low-carbon steels.

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HUMAN HARDWARE

by D. J. Martin

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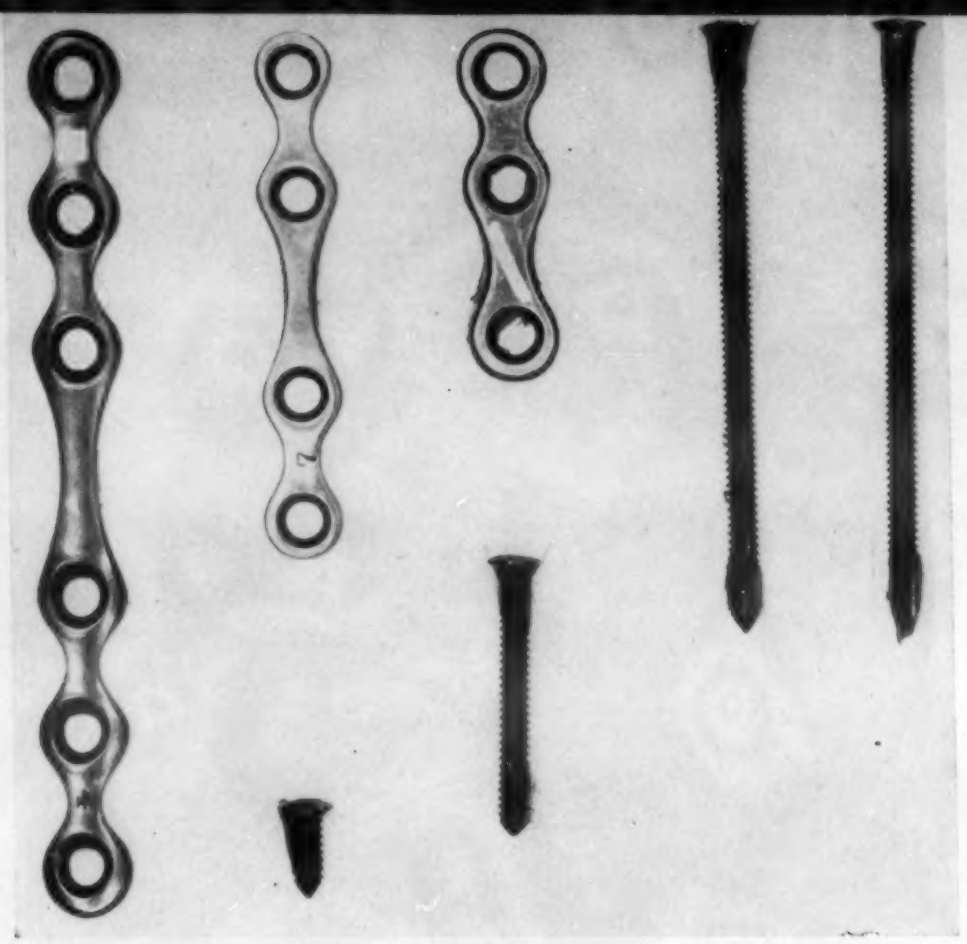


Fig. 1. Steel Bone Plates and Screws—Actual Size.

It would seem that a plain carbon steel of about eutectoid composition, "austempered," ought to be tried for this purpose. The hardness desired is in the range where austempering gives great toughness, as Davenport and co-workers have pointed out. The parts seem thin enough to be within the scope of the austempering process. It would at least be interesting to make some actual parts, such as those shown by Captain Martin and compare the austempered ones with those now used.—H. W. G.

IN THE ORDINARY COURSE OF EVENTS the two ends of a broken bone can be "set," or lined up. The disabled member is immobilized with external splints and bone growth repairs the damage. Such cases are normal when the fracture is at right angles to the axis of the bone and, once set, muscular contraction holds the broken ends together until union takes place. When a bone breaks in such a way that the angle with the axis of the bone is small, muscular pull tends to slide the fragments past each other and an external splint is of little value. This condition is exaggerated in the case of the humerus (one of the bones of the upper arm) and the femur (thigh and ball of the hip joint) because, in these instances, the net muscular force is not parallel with the axis of the bone.

Orthopaedic surgeons have developed a technique for the fixation of such fractures. It involves operation and attachment to the bone fragments of steel plates, screws, pegs, or nails. These bits of metal hold the bone fragments together and in proper alignment until bone growth repairs the fracture. Then, in normal practice, a second operation is performed and the metal is removed because it is considered undesirable to leave these foreign materials in the body.

Occasional failures have been attributed to faulty metal and surgeons' search for the best materials for their needs is not yet ended. That the fault has not always been in the metal used is indicated by the following isolated case: A stainless steel nail was made in two pieces and the head was soldered to the shank. Immersed in body fluids electrolysis separated the two and stainless steel lost favor. However, 18-8 is being used successfully, and Dr. Venable and his associates, from Texas, have recently recommended the use of Vitallium, an alloy of the following composition: Cobalt 65 per cent, chromium 30 per cent, molybdenum 5 per cent, with traces of manganese and silicon.

In 1931 the Fracture Committee of the American College of Surgeons, headed by Dr. Philip D. Wilson of New York, adopted U. S. Bureau of Standards Commercial Standard CS 37-31 for steel bone plates and screws. This pamphlet prescribes the use of SAE 6150, treated to a Rockwell hardness of C 43-53. Surgeons are agreed that it is much better to have a material that will bend than one that will break in service. Hence, the selection of this hardness range, especially in small screws, is open to question. The use of tougher material would seem more desirable.

A few of the 14 standard sizes of plates and the 11 sizes of screws are shown in Fig. 1. The screws are self-tapping and have a centering hole in the head for use with a special self-centering screw driver. Typical photomicrographs of a plate and screw are shown in Figs. 2 and 3. It is apparent that the screw will not meet the hardness specification, Rockwell C 43-53. As a matter of fact the screws are much too small for satisfactory hardness measurement on the standard Rockwell hardness tester. Vickers-Brinell tests (5 and 10 kg. load) on a number of screws gave an

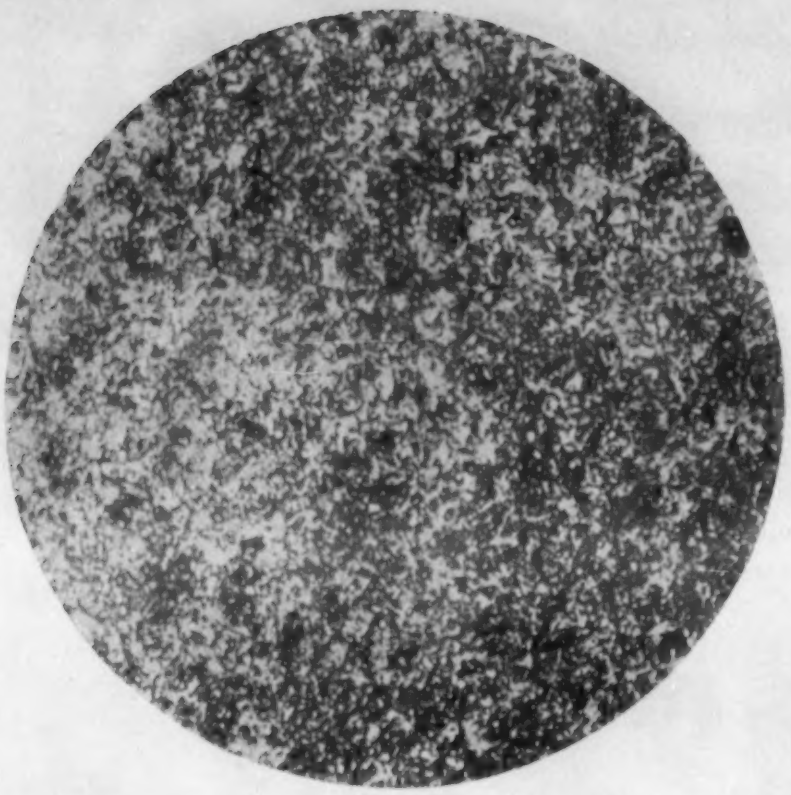


Fig. 2. Photomicrograph of Standard No. 4 Plate. 1000 X.

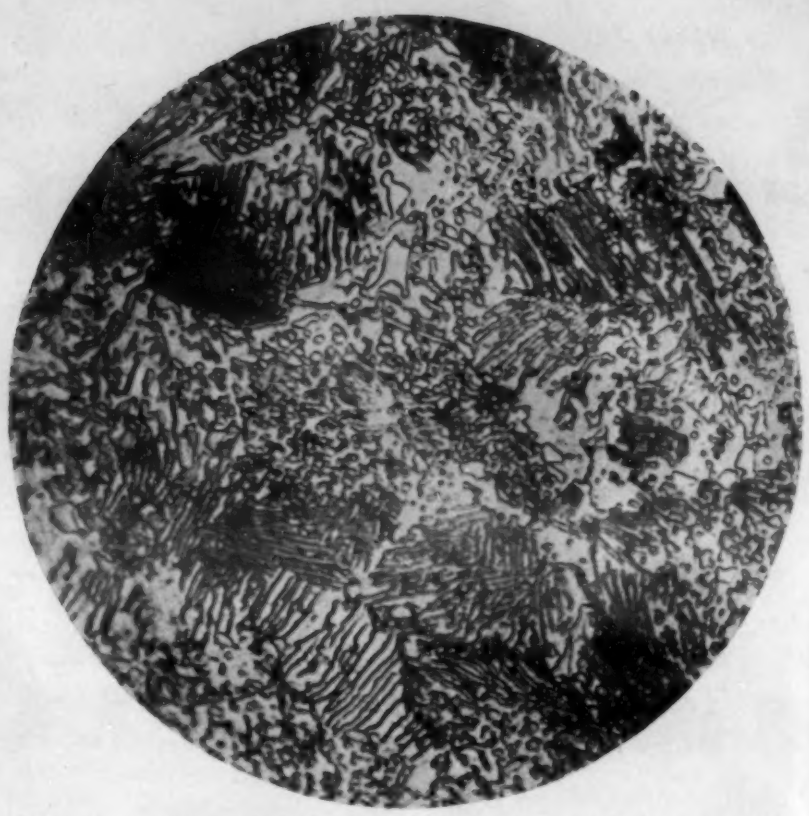
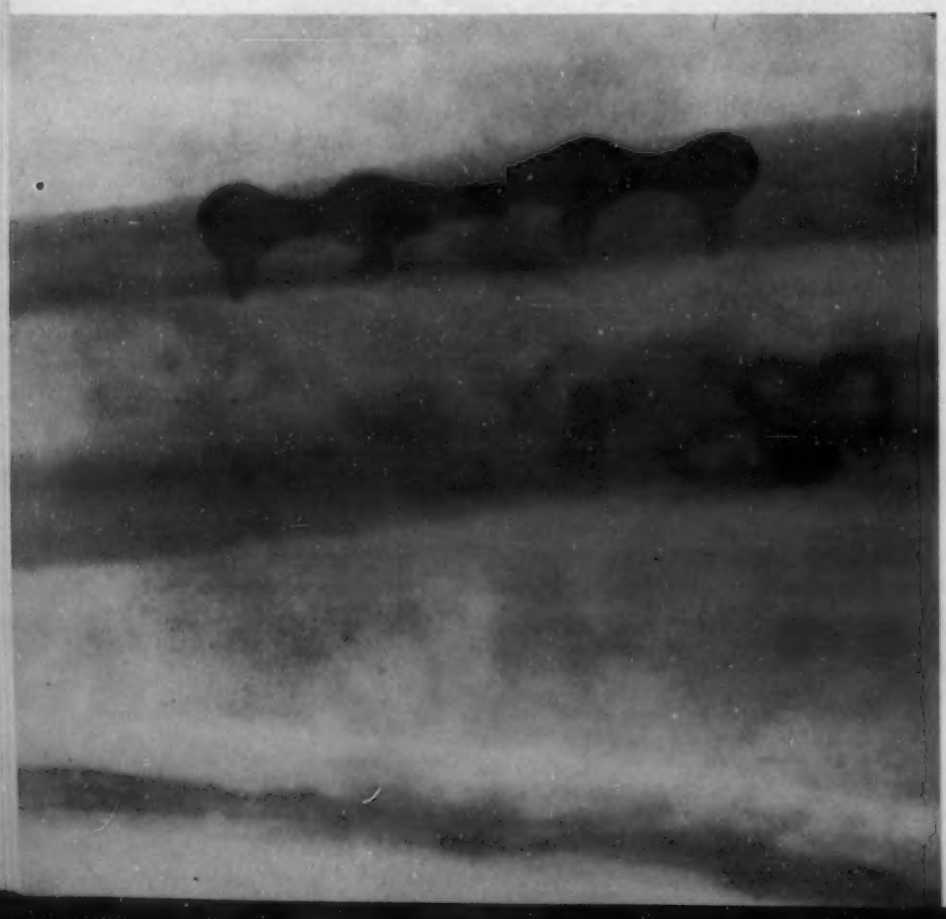


Fig. 3. Photomicrograph of Standard "G" Screw. Partially spheroidized pearlitic structure. 1000 X.

average of 289, which converts to a Rockwell of about C 31. Immediately it will seem fortunate that the manufacturers chose to disregard the requirement for hardness because of the inevitable brittleness of a small long screw with the required Rockwell. Indeed, screws examined after removal from the body as a result of failure in service were always ones that did meet the hardness requirement. On the other hand, dissimilarity in treatment of the plate and screw results in a difference in electrolytic potential which may cause failure when the two are in close proximity in contact with body fluids.

The great majority of the plates used under CS 37-31 have given satisfactory service. They are removed after 9 or 10 months in the body and show no signs of deterioration. Some 5 or 6 per cent do fail, however, and under the circumstances such a percentage is excessive. Failures investigated fall into two classes. In the first, the plate is applied, the injured member is placed in a plaster cast, and an X-ray picture shows that the plate is in good condition. About 8 days later another X-ray photograph shows that the plate has broken. Investigation indicates that plates in this class were cracked in the quenching bath. An example of this type of failure is shown in Fig. 4.

Fig. 4. X-Ray Photograph of Plate Cracked in the Quenching Bath.



The second type of failure is that which normally occurs at the end of 5 or 6 months. CS 37-31 requires that all screw holes be countersunk, and the dimensions given are such that the bottom of the countersink should come less than one half of the way through the thickness of the plate. A straight screw hole should extend from the bottom of the countersink through the rest of the plate. Actually, in most of the plates examined, the countersinking had been carried to the extreme bottom of the hole, leaving a sharp hole with attendant possibilities for high stress concentration.

Although the section across the screw holes is greater than that across the center of the plate, all plates broken in tension break across the screw holes, as shown in Fig. 5. Coupled with this is the fact that some electrolysis takes place between the soft screw and the hard plate. The result is a case of corrosion fatigue. Failures of this type always show a crack system that started at the sharp corner of a screw hole or, occasionally, from the bottom of sharply stamped numbers or other marks of identification on the surface of the plate.

Fig. 5. A Standard No. 7 Plate, Broken through Screw Hole in Tension. Fracture started at sharp inner edge. 10 X.

The author wishes to acknowledge his indebtedness to Dr. Philip D. Wilson. Without his cooperation an understanding of the problems would not have been possible.

EXTRACTION OF OXIDE

Inclusions in High Carbon Iron

— ELECTROLYTIC IODINE METHOD

Part I

by Frank W. Scott

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Inclusions, whether in steel or in cast iron, have been the cause of no little research. Whatever their nature or composition, they may be harmful. A successful determination of their character is important as a means of reducing the number or preventing their presence. The work of Dr. C. H. Herty, Jr., on inclusions in steel is classic and the effect of the results of his studies has been better steel.

These facts apply with equal weight to cast iron. The author of this article reviews briefly some of the methods for determining inclusions and then elaborates on one in particular—the electrolytic iodine—as applied to cast iron. He finds that it is as applicable to cast iron as it is to steel. This may be one step in the improvement of cast iron— a practical result always welcome.—The Editors.

RECENT DEMANDS FOR BETTER cast irons have led to many metallurgical studies concerning the factors affecting their physical properties. It has been known for many years that the pouring temperature, cooling rate, and chemical composition directly affect these properties by affecting the amount, form, and distribution of the carbon. On this basis, cast irons have been graded into (1) pig iron, (2) white cast iron, (3) malleable iron, (4) gray iron. Of these, the production of gray iron castings is of greatest importance.

Foundrymen have observed that the mechanical properties of gray iron may not be the same even with the same chemical composition, pouring temperature, and cooling rate. They have reported that different lots of pig iron will cause a change in the structure of the casting, and that the chilling of castings from coke iron is different than that from charcoal iron. In other words, the finished casting is affected by something in the pig iron from which it has been made that is not shown by the usual chemical analysis.

The mechanical properties that are to be controlled are dependent upon the continuity of the matrix, which is in turn dependent upon the size, distribution and amount of the graphite flakes. Assuming that the foundrymen can control the superheating, cooling rates, and chemical composition, accurately enough to produce uniform castings as regards mechanical properties, certain irregularities are caused by this substance not obtained in the chemical analysis that affects graphitization. At the present time, several hypotheses are under consideration which suggest that the graphitization is dependent upon the presence of non-metallic inclusions which act as nuclei for the formation of the graphite flakes during the freezing of the iron.

Piwowarsky[1] suggested in 1926 that the non-metallic nuclei were particles of graphite that persisted through the cupola melting, and that coarser graphite flakes in the pig produced large graphite flakes noted in the gray iron castings. He later[2] discarded that theory as he found that graphite dissolved readily in the iron when it was remelted.

Von Keil and H. Legat[3] suggested that a sub-microscopic dispersion of iron silicates may act as nuclei to promote graphitization, and to prevent the super-cooled structure. They made the very important observation that it is the size and dispersion of the non-metallics that bring about the fine or coarse graphite structures. Their proposal, known as the silicate slime hypothesis, requires that the iron silicates be so finely divided as to be invisible under the microscope. This hypothesis is analagous to the theory explaining the control of grain size in steel by means of finely dispersed alumina.

J. W. Bolton,[4] and later A. Allison,[5] suggest that perhaps crystals of manganese sulphide may act as nuclei for graphitization, and so they suggest the differences in graphite structure observed between low sulphur Swedish iron, and higher sulphur coke irons are due to these sulphide particles. In a later series of experiments, Norbury and Bolton[6] show that the nuclei effect of manganese sulphide is negligible.

A. Boyles[7] demonstrated that hydrogen may act as a carbide stabilizer, and must be considered as an element affecting the freezing of cast irons. Similar effects were produced by Hanson[8]; Piwowarsky[9]; Bardenheuer and Zeyen,[10] by melting and freezing cast iron under a vacuum and in absence of air or oxidizing gases. These all have a tendency to make cast iron white, and may act similarly in some indirect way such as affecting the amount of oxide present.

Because the oxides are associated with the graphite, and of sub-microscopic size making visual examination impossible, the microscope is of no assistance in their study. This research has been undertaken to develop a method for the extraction of the oxides from foundry iron. To date, the opinion that the inclusion nuclei theory explains the variation of graphitization characteristics of cast iron is purely a hypothesis with almost no data to substantiate it, and only limited circumstantial evidence. With the development of a method for the determination of these oxides, experimental data may be obtained that will enable the metallurgist to understand the phenomenon under consideration.

RESUMÉ OF LITERATURE

AN INVESTIGATION into the subject of non-metallic inclusions in ferrous materials reveals that hundreds and perhaps several thousand papers have been written concerning their source, methods of analysis, and their effects. An extremely comprehensive bibliography[11] has been published covering publications to 1934 inclusive. Further publications have appeared since then. In this resumé an attempt will be made to familiarize the reader to some extent with the history of the work that has been done, and the present day status of the various methods for oxide and oxygen determination.

The Aqueous Iodine Method

In 1853, before the days of steel production, Morfit and Booth[12] suggested the use of an iodine solution in water to separate the slag residue from metallics. The iodine method was again suggested in 1868 by V. Eggertz,[13] and today the aqueous iodine method is usually referred to as the Eggertz method.

The next outstanding publication was by Westcott, Eckert, and Einert,[14] who in 1927 described a critical study of its application to the study of slag in wrought iron. They studied the solubility of the oxides in the iodine solution and in the solutions used in washing the oxide residue, and concluded that good results could be obtained with proper procedure.

The next paper of importance was published by Cunningham and Price[15] in 1933. They proposed to modify the iodine method by preparing an iodine solution in ferrous iodide, containing ammonium citrate, and then to dissolve the steel in this solution. The proposed procedure was fairly rapid, and with its ease of application it was hoped it would be popular with the steel maker.

The Alcoholic Iodine Method

Certain oxides, manganous oxide in particular, is known to be soluble in the aqueous iodine solution method. This is believed to be due to the increasing acidity of the solution containing high concentrations of ferrous iodide. Also, it appears that some HI is formed during the reaction of metal and iodine in the aqueous solution. To overcome this difficulty, Williams[16] in 1928 suggested the use of dry alcohol instead of water as the medium. His results indicated that the recovery of MnO was definitely improved. In 1935, Rooney and Stapleton[17] described a method using water free alcohol and iodine to dissolve the steel and to recover the oxides. They designed a very ingenious set-up to extract the oxides and to filter them under controlled atmospheres.

Acid Solution Methods

In 1905, J. E. Stead[18] dissolved steel in dilute nitric acid, and collected the residue. Later, in 1926, J. H. S. Dickenson[19] described the nitric acid solution method and the method has since been referred to as the *Dickenson* method. The results of a critical study of the Dickenson method were published in 1928 by C. H. Herty, Jr.,[20] and a modified procedure given. It was shown that only the pure silica and alumina were recovered appreciably, while iron and manganese silicates and aluminates, and the purer iron and manganese oxides were partially or totally dissolved.

In 1915, F. O. Kichline[21] described a method for the determination of aluminum oxide in steel by separation of the oxide using dilute hydrochloric acid to dissolve the steel. In 1932, J. G. Thompson and J. S. Acken[22] published the procedure used at the Bureau of Standards for the determination of silica, as well as alumina, using dilute hydrochloric acid to effect the separation of metallic and oxide constituents. They show that this method compares favorably with the Dickenson method, and is preferred on grounds of speed and simplicity.

Bromine and Chlorine Solution Method

In 1881, W. Bettel[23] used bromine in aqueous solution to remove the metallic portions from the oxides. Due to the serious loss of the oxides soluble in it, as it is quite acid in character, and the difficulty in handling it, the bromine method is rarely used today.

R. Fresenius[24] is credited with the discovery that when a sample of iron is heated several hours at a moderate temperature, 350 to 500 deg. C., in a stream of chlorine gas, the metallic constituents are converted into chlorides, which are volatilized, leaving behind the oxides. At the present time, only SiO_2 and Al_2O_3 are determined by this method, as FeO and MnO are lost to a considerable extent by the chlorine attack.

Several other methods have been suggested using ferric chloride, cuprous ammonium chloride, and mercuric chloride, but these methods are not used today.

Electrolytic Methods

The principle of the electrolytic method of oxide extraction is the same as the simple solution extraction of oxides in that the metallic constituents are separated from the non-metallics, and the oxides are determined in the non-metallic residue. The sample is the anode in the cell,

and the electrolyte should be such as will decompose all other non-metallics, excepting the oxides. The oxide residue must be washed to free it of any contaminating material, and then analyzed.

In 1929, C. H. Herty, Jr.[25] published a paper concerning the theoretical aspects of obtaining the slag residue by electrolyzing the steel, and collecting the slag-carbon residue. Following the publication of this dissertation, several methods have been prepared, differing in the electrolytes proposed.

G. R. Fitterer,[26] in 1931, described an electrolytic method for the analysis of both oxides and sulphides using a $FeSO_4$ + NaCl electrolyte. Iron oxide could not be determined due to the voluminous precipitate of iron hydroxide during the electrolysis. Recent work has shown the hydrolysis of other metals, and the presence of carbides and silicic acid in the residue.

In 1932, F. W. Scott[27] proposed to combine the good properties of the iodine solution method with the desirable properties of electrolytic extraction. He proposed the use of a MgI_2 electrolyte to extract the oxides only. More will be said about this procedure later. Hare and Soler[28] applied a similar method.

R. Treje and C. Benedicks,[29] in 1932, proposed the use of an electrolyte of sodium citrate and potassium bromide for oxide and sulphide extraction. The method was to be used on low carbon iron only as the carbides were not decomposed. Also, the electrolyte increased in acidity during the electrolysis, limiting the time, and so limiting the size of sample that could be extracted. A study of the method indicated that the sulphides are not quantitatively recovered, that the residue contains metallics, that the acid electrolyte dissolves some MnO, and that silicon treated steels have silicic acid in the residue. Satisfactory results for silica and alumina in rimming steels have been obtained.

H. Styri,[30] in 1933, published the results of a series of experiments in which he used an acid electrolyte for the extraction of oxides and sulphides. He believes that an acid electrolyte sufficiently acid to prevent hydrolysis is desirable, and only a moderate solubility of the purer MnO and FeO inclusions occur. Principally his method is applicable to silica and alumina.

Hydrogen Reduction Method

In 1872, A. Bender[31] passed a stream of hydrogen over hot iron, and determined its oxygen content, probably the iron oxide content, by weighing the water formed. Later, in 1882, Ledebur[32] wrote the description of the hydrogen reduction method as applied to wrought iron, and the method is generally referred to as the Ledebur method today.

In 1919, Cain and Pettijohn[33] made an exhaustive study of the hydrogen reduction method. They were convinced that the errors entering into the procedure due to sampling, incomplete reduction, and manipulation prevented accurate analysis.

The latest publication concerning oxygen determination by hydrogen reduction appeared in 1934, by Brower, Larsen and Schenk,[34] and they modified the procedure radically.

Vacuum Fusion Method

In 1912, Walker and Patrick[35] described a method of oxygen determination in which the sample was melted under a vacuum in a carbon crucible, and the carbon reduced the oxides. The resulting gas was recovered and analyzed, giving a figure for total oxygen present in the steel or iron.

In 1921, Vacher and Jordan[36] studied the method and found it gave good results for oxygen, nitrogen and for hydrogen. Certain errors were observed to occur and precautions were outlined to obtain good results.

In 1935, J. Chipman and M. G. Fontana[37] published a paper giving several improvements in the apparatus used in the vacuum fusion method. They had a low blank, very high vacuum, and consistent results.

SUMMARY AND DISCUSSION

AFTER over 80 yrs. of study, and all the research that has been done, chemists and metallurgists do not agree that any one method is most accurate, and can be relied upon to give good results under all conditions. As most all the work has been done on steel or low carbon products, this feeling is mostly expressed when pig or cast irons are considered. At the present, chemists are divided in preference between "hot" and "wet" methods.

The "hot" methods depend upon the reduction of the oxide substances at high temperatures by either carbon or hydrogen, with the determination of the resulting compound, CO_2 or H_2O. The vacuum fusion, or carbon reduction, method is regarded with some favor at the present time, and is considered to be reliable for *total* oxygen determination. There are several chemists and metallurgists that believe that the hydrogen reduction method is the best for this determination. The results obtained by the two methods do not check when applied to the same sample, and this is not explainable at this time. The oxygen determined by these methods includes any gases entrapped in blowholes, any CO dissolved in the metal, and the oxygen combined as oxides. These procedures do not give any information as to *how* the oxygen is present, only *how much* is present.

The "wet" methods endeavor to dissolve the metallic iron from the oxides, leaving the oxides as a residue. This entails the decomposition of other non-metallics, as carbides, sulphides, phosphides, hydrides, etc., without the solution or decomposition of the oxides. In these residue methods we find three different types of procedures: (1) a direct solution of the metallic constituents in aqueous or alcoholic solutions; (2) a solution of the metallic constituents using the sample as the anode in an electrolytic cell, separating the insoluble oxides from the metallic portions; (3) heating a sample of steel or iron in a stream of chlorine gas at an elevated temperature, volatilizing the metallic constituents as chlorides, and leaving behind the residue of oxides.

Results obtained on the same iron or steel by the various methods show great discrepancies both in amount and composition of the oxide particles, and some intensive critical studies have been made to explain why these occur. In the "wet" methods, these discrepancies have three sources: (1) the various solutions used by the different methods

dissolve not only the metallic portions but certain of the oxides, either totally or in part; (2) the various solutions do not decompose completely all the non-metallics, and some of the carbides, sulphides or phosphides may be present with the oxides giving an apparent high oxide residue; (3) some solvents oxidize the metallic portions, or partially oxidize them in presence of air, and, instead of being in solution, they are collected with the oxide residue. However, the reader must not understand that these methods have not yielded some very useful and valuable information in the study of residues in steel. The fact is that the iodine method is giving some very valuable information as to the cleanliness of deoxidized steels, especially in the low carbon ranges.

In 1933, a project was sponsored jointly by the National Bureau of Standards and the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers, to submit identical samples of steel to a number of laboratories for oxygen analysis by different methods. The former prepared and distributed the samples of plain carbon steels, and collected the data. In all, 34 laboratories participated, submitted results by the methods as follows: 15 determinations of the eight samples by the vacuum fusion method, 11 reports by the iodine method, 7 reports by electrolytic methods, 4 reports by the hydrogen reduction method, 3 reports by the chlorine method, 2 by the mercuric chloride method, and one each by the nitric acid and hydrochloric acid methods. These reports contained over 2000 analytical determinations, which were tabulated, studied by several committees, and the results published by Thompson, Vacher and Bright.[38]

Following a detailed study of the results submitted by as representative a group of analysts as it was possible to engage on the problem, the authors commented that "The first impression derived from a study of the data of these cooperative analyses usually is that the results as a whole are decidedly unsatisfactory and indicate that none of the methods for determining oxygen or oxides is sufficiently accurate to conform to the requirements of modern metallurgical analysis." Then they stated that because of the fact that the amounts of substances being determined are very small, and that the accuracy of the chemical analysis is affected by this small amount of material, the cooperative results are fairly satisfactory. From the results submitted, best agreement among themselves was observed among the users of the vacuum fusion method, and it was concluded that this method yielded the best results on all samples. The residue methods, the aqueous-iodine method being most prominent, yielded accurate results on deoxidized steels, but low results on rimming types. The few results submitted by the operators of the hydrogen reduction method indicated that more standardization of the procedure was desirable. Also they suggested further standardization of the residue methods.

Considering all the methods available, it appears that the electrolytic method of extraction offers several distinct advantages in studying the oxides in pig and cast irons: (1) a large, and hence a more representative, sample is obtained; (2) the composition of the oxides may be determined on the larger residue by standard analytical procedures; (3) the equipment is simple and inexpensive, and the cost of chemical reagents moderate; (4) consistent results are obtainable on all carbon ranges.

[The concluding portion of this article will deal with the effect of the analysis of iron alloys on oxide extraction together with photomicrographs. The method recommended for extraction and analysis of oxides from high carbon iron will be included.—*Editor.*]

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DETERMINATION OF

BORON IN STEEL

BY SPECIAL ORGANIC REAGENTS

by H. A. Kar

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Although boron is still somewhat of a stranger within our metallurgical gates, its possibilities are being probed in several directions, and some interesting applications are already in sight. It has been recommended as a constituent of cutting alloys, as a minor ingredient of aluminum-copper alloys for refrigeration service, and as an addition to copper-silver-cadmium electrical contacts. Hardfacing alloy rod has been prepared with boron as an important ingredient. The addition of metallic borides to cast iron and steel during melting has recently been recommended as a method of producing very hard, abrasion resistant materials, which are claimed to be weldable without an applied flux because of the fluxing action of boron compounds produced on the surface during heating.

Whatever the merit of these individual proposals, interest in boron is not lagging, and it is clear that accurate, convenient methods for determining this element will be welcomed by the analytical chemist and development engineer alike. This article is the third by Mr. Kar that we have published in recent years. In each case we have stepped outside of our nominal field into that of the chemist because the particular analytical advance reported was of more than ordinary interest to the metallurgical industry.—The Editors.

THE DETERMINATION OF SMALL AMOUNTS of boron (usually between 0.001 per cent and 0.03 per cent) introduced in steel for experimental purposes, has been a difficult analytical problem. A recent survey of the literature, followed by considerable laboratory work, has resulted in a short and dependable method for the identification and estimation of the small amount of boron present in such steel. By this method a boron analysis can be completed in a reasonable length of time with consistent results, particularly with the quinalizarin test as outlined below.

Former Methods

The commonly used methods for boron determination are those of Chapin, Lindgren, and Tschischewski. Chapin's method[4] depends upon the solution of 1 g. of steel in dilute hydrochloric acid under a reflux condenser, oxidizing with hydrogen peroxide and volatilizing the boron with methyl alcohol by several distillations. After evaporating the alcohol in the distillate, the solution is titrated with standard sodium hydroxide. This method is subject to an error of 0.03 per cent.

Lindgren's method[4] calls for dissolving 3 g. of steel in equal portions of nitric and hydrochloric acid (20 cc. in all and neutralizing with calcium carbonate (usually about 30 g. of $CaCO_3$). After boiling off all carbon dioxide, the precipitate is filtered and the boron in the filtrate is titrated with standard sodium hydroxide.

Tschischewski's method[4] requires dissolving the steel in dilute sulphuric acid under a reflux condenser, oxidizing with hydrogen peroxide and separating the iron, manganese, etc., by electrolyzing the solution with the mercury cathode.

Chapin's method is long and tedious and the accurate determination of a very small amount of boron when using a 1-g. sample is improbable, inasmuch as the method is subject to a 0.03 per cent error. Lindgren's method is open to the objection that such a small amount of boron in the large mass of precipitate made by 3 g. of iron and 30 g. of calcium carbonate presents a difficult analytical problem. The Tschischewski method does not function satisfactorily because of the presence of sulphate ions in the solution.

Furthermore, the final estimation of boron by sodium hydroxide titration as suggested in these methods does not yield consistent results, as the blank is occasionally equivalent to ten times the boron content. The blank is due to carbon dioxide, which may be present in the water and especially in the sodium hydroxide.

Other Tests

Several other tests mentioned in the literature have also been studied. These tests were devised for the sole pur-

General View in Timken Chemical Laboratory

pose of detecting boron in non-ferrous compounds or minerals. Among the procedures found in the literature, the turmeric paper, quinalizarin, and curcumin tests are most promising.

The turmeric paper test, devised by W. H. Low[1], calls for distilling the boron by Chapin's method and dipping a strip of turmeric paper in the distillate in a graduated cylinder for a certain length of time, then comparing the color with that of a standard. The basis of the test is the depth of coloration (red) imparted to the upper end of the turmeric paper by the solution drawn up by capillary action to the exposed end of the paper. The use of the Chapin method for separating the boron by distillation is open to the objection stated previously.

The quinalizarin test, devised by Feigl and Krumholz,[2] calls for adding one drop of the reagent dissolved in concentrated sulphuric acid to the residue, which may either be dry or in a concentrated sulphuric acid solution. A change in color from purple to blue indicates the presence of boron.

The curcumin test, devised by Cassal and Gevrans,[6] calls for adding oxalic acid and an alcoholic solution of curcumin to the slightly hydrochloric acid solution of the substance. By evaporating the substance to dryness a red color imparted to the mass indicates the presence of boron.

Laboratory investigation has developed the application of the quinalizarin and curcumin tests to the determination of boron in steel by the procedures outlined below.

Procedure for Quinalizarin Test

The quinalizarin reagent used in this test is prepared simply by adding 5 mg. of quinalizarin to 100 cc. of concentrated sulphuric acid and stirring. The actual procedure used in determining boron in steel is as follows:

> Transfer 1 g. of the steel to be analyzed to a 500 cc. flask and add 15 cc. of 1:5 sulphuric acid. Heat on an electric plate under a reflux condenser until the action is complete. Oxidize with 2 cc. of 3% hydrogen peroxide poured through the condenser and boil for 15 min. Cool, filter and electrolyze by a mercury cathode[7] to separate the iron, manganese, chromium, etc. Filter the acid solution, add 10 cc. of concentrated sulphuric acid to the filtrate and evaporate to fumes. Cool and pour the solution into a 100 cc. graduate. Add 5 cc. of quinalizarin reagent solution, dilute to 100 cc. with concentrated sulphuric acid and mix. Place the graduate on a white marble slab or other suitable background and compare the color with a standard (described below) by the reflected light from a daylight lamp located behind the tube.

The comparison standard for use in the quinalizarin test should be prepared as follows:

> Transfer 1 g. of boron-free steel to a 500 cc. flask, add 5.7 mg. of C.P. boric acid and 15 cc. of 1:5 sulphuric acid. Heat under a reflux condenser and proceed in the same manner as described above until the electrolyzed sample is evaporated to fumes. Cool and dilute to 95 cc. with concentrated sulphuric acid. Each cc. of this solution will contain 0.001% boron. Add 5 cc. of the quinalizarin reagent solution and mix. Transfer to a Nessler tube and compare the color with that of the unknown.

Special Aspects of the Quinalizarin Test

Beryllium and magnesium interfere with this determination, as quinalizarin reacts with these elements.

The determination can be made only in concentrated sulphuric acid; other acids produce no color with quinalizarin.

Iron, manganese, chromium, etc., do not affect the color so long as boron is present and the steel solution is in concentrated sulphuric acid.

Keeping ferric sulphate clear in solution in concentrated sulphuric acid is difficult. To obtain a clear solution in concentrated sulphuric acid the iron and other constituents of the steel must be removed, preferably by electrolysis.

The same volume of quinalizarin solution must be used for all determinations. A quinalizarin blank in a separate tube must be used to verify the change of colors from plain purple (color of quinalizarin in concentrated sulphuric acid) to light blue and then to deeper blue. The purple color begins to disappear at 0.008 per cent boron and the solution assumes a light blue color at 0.01 per cent boron. Deeper blue colors will be observed when the sample contains more than 0.01 per cent boron.

The quinalizarin test for boron in steel is simple and rapid. The color change is so sharp that the presence of 0.001 per cent boron in the quinalizarin solution can be noticed easily.

Procedure for Curcumin Test

The curcumin reagent used in this test is prepared in the following way: Add 100 mg. of curcumin to 100 cc. of 95 per cent ethyl alcohol in a stoppered bottle and shake to dissolve. Allow to settle overnight and filter. The application of this reagent to the determination of boron in steel is as follows:

> Transfer 2 g. of the steel to a 500 cc. flask and add 25 cc. of 1:1 hydrochloric acid. Heat on an electric plate under a reflux condenser until the action is complete. Oxidize with one or two crystals of potassium chlorate dropped through the condenser and boil for 15 min. Cool and transfer the solution to a flat bottom platinum dish. Add 10 per cent sodium hydroxide, prepared in another platinum dish, until the solution is alkaline and add 5 cc. in excess. Boil 1 min. and allow to cool. Dilute to

Battery of Mercury Cathode Equipment in Timken Chemical Laboratory

200 cc. and mix thoroughly by pouring from one platinum dish into the other 4 or 5 times. Filter 100 cc. (equivalent to a 1-g. portion) into a platinum dish and acidify with hydrochloric acid. Transfer the solution to a new casserole and add 0.5 g. of oxalic acid. Add 0.5 cc. of curcumin solution for each estimated 0.01 per cent of boron present and evaporate to dryness on a steam bath.

The color of the dried mass at this stage is important. A white color with a yellow cast indicates the absence of boron, while a red color indicates its presence. If too much curcumin is used, a definite orange shade appears. In this case, the portion must be discarded and the operation repeated on the remaining aliquot, using less curcumin.

If the red color appears, cool and dissolve the salts in 100 cc. of cold distilled water. Filter and wash with cold water. Discard the filtrate and place a 100 cc. graduate under the funnel. Add 10 cc. of 95 per cent ethyl alcohol to the residue in the casserole, agitate to dissolve and transfer to the filter paper. Repeat this operation 3 or 4 times to wash all the colored boron compound out of the casserole and filter paper. Dilute with alcohol to 50 or 100 cc. and compare the color with a standard (described below) in a colorimeter.

The comparison standard for the curcumin test is prepared as follows:

Transfer 2 g. of boron-free steel of the same general composition as the one being tested to a 500 cc. flask, add 25 cc. of 1:1 hydrochloric acid and 5.7 mg. of C.P. boric acid (equivalent to 1 mg. of boron). Heat to dissolve and proceed as described above until the solution is evaporated to dryness. Take up with alcohol and compare the color with the unknown in a colorimeter. If desired, a series of standard colors may be prepared by dilution, using 0.002 per cent boron as gradations.

Special Aspects of Curcumin Test

Iron, manganese, chromium, etc., must be removed by sodium hydroxide because they mask the color of red boron compounds. Sulfates must be absent as they destroy the red color when evaporated to dryness. Chlorides do no harm, and a slightly acid HCl solution is the most favorable medium for the action of curcumin with boron in the presence of oxalic acid. Beryllium must also be absent because curcumin reacts in the same manner with it as with boron.

Selection of the dishes to be used for boron determinations is important. Practically all glass and porcelain ware contains boron. Therefore, alkaline solutions must not be placed in such dishes. Flat platinum dishes are most suitable for this kind of work. Final evaporation of slightly acid solutions can be made in new casseroles.

The use of curcumin must be controlled so that any excess will be avoided. Curcumin does not combine with sodium salts. Excess of curcumin will separate out in its original state by evaporation; both the curcumin and boron compound will dissolve in alcohol and thus will dilute the color because the color of curcumin is orange yellow in alcohol and the color of boron is deep red in alcohol.

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PRODUCTION DATA OF THE

Steel Foundry Industry

FOR 1937

By E. F. Cone

IT MAY BE REMEMBERED that in an article in the April, 1937, issue of METALS AND ALLOYS, on page 111, entitled "Production Data of the Steel Foundry Industry," attention was called to the fact that no complete data are published of the quantity of steel castings produced by the American steel foundry industry.

No Complete Statistics Since 1933

It was pointed out that the statistics of the American Iron and Steel Institute, valuable and accurate as they are, have not since 1933 included returns from the steel casting industry as a whole in the Institute's record of the country's steel production. This is due to the fact that, with the establishing of Codes of Fair Practice under the NRA and the formation of such organizations as the Alloy Casting Association, the Manganese Steel Founders' Society and so on, the Institute left the assembling of such data to these organizations, including the Steel Founders' Society of America which had been in existence for some 36 odd years and still is active in that field. Therefore the data of the A. I. & S. Institute furnish only the steel casting output of ingot producing companies making their own castings. It is thus quite evident that complete data of the steel foundry industry's production of castings as a whole are not available in published form.

Production Data for Last Four Years

Last year, because of the helpful cooperation of the Steel Founders' Society of America, the writer was able to publish that organization's production data and from these to estimate, fairly accurately, the country's steel foundry production. Again this year the S. F. S. A. has cooperated and furnished its 1937 data.

The statistics of this society are presented in three different calculations: (1) Total data as collected by this society; (2) estimated output of all producers on the basis of the society's statistics representing 95 per cent of the total miscellaneous and special commercial castings; and (3) the estimated production of the foregoing plus the output of those companies which produce castings for their own use, such as the large machinery builders, the electrical equipment companies and some of the large steel working companies. This figure is arrived at on the basis that the data represented by (1) and (2) are 83 per cent of the country's total, according to the experience of the S. F. S. A. over a period of years. On this basis the data for the last 4 yrs. are found in Table I.

Table I.—Output of Miscellaneous and Special Commercial Castings in Net Tons

	S. F. S. A.	Total *	Including Castings for Use *
1934	375,122	395,000	476,000
1935	368,851	388,200	467,700
1936	718,068	755,800	910,000
1937	907,674	955,400	1,151,100

* Estimated.

Large Increase in 1937

According to the data in Table I, the 1937 production of miscellaneous and special commercial steel castings was 955,400 net tons and the total for the country, including the castings which companies make for their own use and not for sale on the market, was 1,151,000 net tons. A very pronounced increase was thus registered last year, continuing the rather remarkable recovery which took place in 1936. The 1937 output of 907,674 net tons reveals an increase of 26.3 per cent over 1936 and one of 145 per cent over the 368,851 net tons in 1935.

It is to be regretted that the foregoing data are not segregated so as to differentiate the alloy steel production which was available from the Institute, previous to 1934.

Table II.—American Steel Casting Output in Gross Tons

	Castings	Alloy	Alloy, Per cent
1921	559,713	40,255	7.2
1926	1,357,558	146,101	10.7
1929	1,583,040	192,920	12.2
1930	1,104,215	126,128	11.5
1931	516,579	89,903	17.4
1932	216,760	41,044	18.8
1933	838,061	71,783	21.2
1934	425,000*	61,625†	14.5
1935	417,600*	64,700†	15.5
1936	812,500*	134,000†	16.5
1937	1,027,800*	159,300†	15.5

* S. F. S. A. data in Col. 3, Table I, in Gross Tons.
† Estimated.

Figuring the data in the third column of Table I to gross tons, some of the data previous to 1934 and the total steel castings output for the last 4 yrs. are found in Table II.

(Concluded on page 181)

The Hydride Process — III

— TITANIUM SILICIDES

by Peter P. Alexander

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Part I of the first published presentation of this new and important metallurgical development appeared in METALS AND ALLOYS, Vol. 8, September, 1937, page 263. Part II was published in Vol. 9, February, 1938, page 45 and dealt with the preparation and properties of titanium hydride and the production of Cu-Ti alloys.

TITANIUM FORMS, with certain elements, compounds of extreme hardness some of which, such as titanium carbide, have already industrial applications. Yet the properties of other compounds of titanium deserve investigation also as they might find useful applications.

Early Work on Hard Titanium Compounds

The pioneer work on the production of hard titanium compounds was done by Prof. Henri Moissan shortly after his invention of the electric furnace. During his fundamental researches, Professor Moissan,[1] among other compounds, prepared titanium carbide, titanium nitride, titanium silicide and titanium boride.

Titanium carbide was produced by the reduction in the electric furnace of titanium oxide with carbon. Although this compound burns in air at high temperature even more readily than pure titanium metal, yet Professor Moissan succeeded in preparing it. His first experimental electric furnace consisted of two blocks of calcium oxide tightly fitted one to another, one block forming the top and the other the bottom of the electric furnace. The graphite electrodes were fitted through the holes machined through the calcium oxide blocks and the hearth itself was only a cavity of small dimensions carved in the middle of the calcium oxide blocks so that it was entirely protected from the air. During the operation of the furnace the gases resulting from the arc flame were creating a pressure inside of the furnace greater than the atmospheric pressure, so that the air was entirely eliminated from the furnace during the melting operation. When the same furnace was used for the production of other compounds of titanium, the resulting products of course were contaminated with carbon. For instance, the titanium produced in that furnace contained only 94 to 96 per cent of titanium, the balance being carbon.

The exact ratio between titanium and the alloying element was varying in appreciable limits during various runs. Yet the results obtained indicated that three compounds, namely titanium silicide, titanium nitride and titanium boride, possessed very great hardness and could be used to advantage n applications where such a quality is desirable. Titanium nitride, for instance, as stated by Professor Moissan,[2] was hard enough to scratch rubies and even slowly cut diamonds. Titanium silicide was also found to be of the same hardness as diamonds. In fact, it was recommended later by G. Gin[3] for the polishing of precious stones.

Hardness of Titanium Silicide

The hardness of titanium silicide, however, was found by other investigators to vary considerably in accordance with the method used in its preparation. Titanium at high temperature has a very high affinity for oxygen and N so that in order to protect this metal from contamination during the preparation of the compound, it is usually necessary to use a large excess of silicon to absorb all traces of air which may infilter into the furnace. The resulting product, therefore, varies somewhat in composition and hardness.

Titanium silicide was accidentally prepared for the first time, even before the experiments of Professor Moissan, by L. Levy[4] who, in attempting to produce pure titanium metal, was passing the vapors of titanium tetrachloride in a stream of hydrogen over the incandescent silicon. As a result of this treatment, he obtained white cubic crystals of considerable hardness. The analysis of his product indicated that the above crystals contained only about 80 per cent of titanium. Yet Levy did not recognize the fact that he had produced titanium silicide, represented by the formula Ti_2Si, and believed that his product was impure titanium.

Therefore, Professor Moissan should be given credit as the first to prepare titanium silicide which the analysis in-

Fig. 1.—Structure of Sintered Titanium. Etched with 5% HF. 500 X.

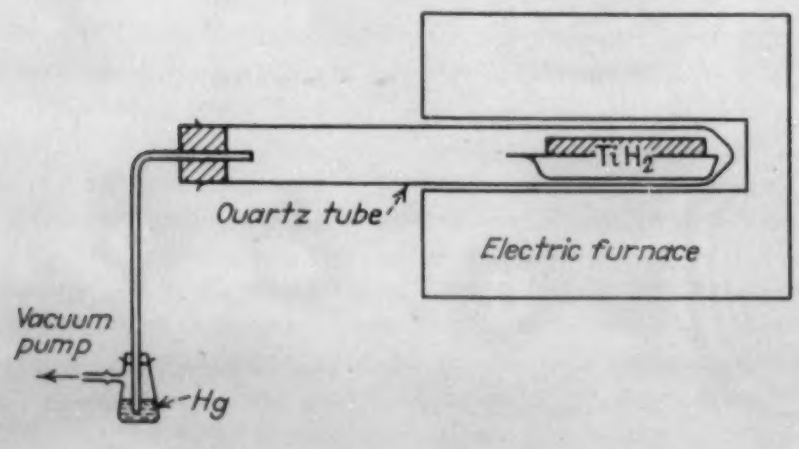
dicated as containing titanium and silicon in their molal proportions and which Professor Moissan represented by the formula TiSi.

By using a modified alumino-thermic method, described by Holeman,[5] and further modified by O. Honingschmid,[6] another silicide of titanium was prepared. As described by Dr. Honingschmid, he used a mixture of fluosilicate of potassium and double fluoride of titanium and potassium mixed with powdered aluminum and all covered with a layer of powdered magnesium. He obtained titanium silicide which came in the form of iron-gray crystals of tetrahedral pyramids. He found that this silicide which answered the formula of $TiSi_2$, had a hardness which varied from 4 to 5, that is, less than that of feldspar. Like the titanium silicide prepared by Professor Moissan, it resisted attack of all acids except hydrofluoric, and was oxidized only with great difficulty even in the flame of a Bunsen burner.

Three Titanium Silicides

The three silicides, Ti_2Si, TiSi and $TiSi_2$, prepared by the above investigators, possess different degrees of hardness, and if the highest hardness is desirable it is necessary that the combining weights of the elements should be carefully proportioned since either an excess or a deficiency of silicon in the resulting material would produce a silicide of much lower hardness.

Fig. 2.—Laboratory Apparatus for Sintering in Nascent Hydrogen.



Titanium Silicide by the Hydride Process

In preparing these compounds by the Hydride process, that is, by the use of titanium hydride, it is possible to eliminate all the possibilities of contamination of the charge with oxygen of the air and therefore avoid all losses either of titanium or silicon. This is due to the fact that, during the heat treatment, titanium hydride decomposes into metallic titanium and nascent hydrogen, which creates a protective atmosphere around the charge and facilitates the alloying of the elements in the charge. The ease of alloying in the atmosphere of nascent hydrogen can be seen from the fact that pure titanium metal which has a melting point of over 1800 deg. C. in an atmosphere of nascent hydrogen, can be sintered into a compact mass at a temperature as low as 900 deg. C. (See Fig. 1)

When titanium hydride is used for the production of pure titanium metal, the powdered hydride which comes in the form of extremely fine powder of less than 300 mesh, is pressed into briquettes and heated in a vacuum furnace to temperatures above the dissociation of titanium hydride, that is above 400 to 500 deg. C. As soon as the hydrogen begins to evolve, the vacuum pump may be stopped and the retort filled in a few minutes with hydrogen evolving from the hydride. The further increase of temperature of course results in the additional evolution of hydrogen and in the increase of pressure in the retort. Yet the pressure of the gas inside of the retort can be automatically regulated either by a safety valve or a simple mercury overflow valve. By this means the charge in the retort produces its own atmosphere of pure hydrogen which facilitates the process of sintering and prevents the infiltration of air.

Hydrides as a Source of Pure Hydrogen

In a similar manner the metallic hydrides could be used in other operations as sources of 100 per cent pure hydrogen. Indeed, it is only sufficient to place a small amount of metallic hydride in the retort, heat the same until the hydrogen will begin to evolve from the hydride which would exclude all possibility of contamination of the charge in the retort. During the cooling of the retort the partly dissociated metallic hydride will re-absorb all the hydrogen in the retort and create a vacuum so that the cooling is produced in vacuum. However, if it is desired to cool the contents of the retort in a hydrogen atmosphere, the metallic hydride should be placed in a separate retort maintained during the cooling of the first retort at high temperature.

Thus, by varying the technique of using a metallic hydride, the operations could be carried on either in vacuum or in pure hydrogen. This method seems to be especially suitable for use in laboratories.

Titanium, freshly liberated from the hydride in an atmosphere of 100 per cent pure hydrogen, sinters so readily that even a temperature as low as 900 deg. C. is sufficient to produce complete sintering of the powdered material into a solid briquette.

Such compact, sintered titanium is not attacked by hydrochloric acid and resists oxidation even at high temperature quite well. In fact, small slabs of sintered titanium could be heated in a Bunsen burner to incandescence without any change. Only the surface will be covered with a very thin layer of adherent oxide.

The same procedure is used in the production of titanium compounds such as titanium silicide. The powdered materials in the exact ratio are thoroughly mixed, pressed into briquettes and placed in the retort. The vacuum is maintained as in the case of the sintering of pure titanium, only until the beginning of the active evolution of hydrogen from the titanium hydride. From then on the operation is conducted, as in the first place, in an atmosphere of hydrogen.

Since all the conditions during this operation can be rigidly controlled, the titanium silicide can be obtained in any desired form. For instance, if the temperature is not allowed to rise too high, the produced silicide comes in the form of a very fine sponge which can be readily crushed to a powder of any desired degree of fineness by ordinary methods. The titanium silicide produced by this process even in spongy form is hard enough to easily scratch quartz and even sintered tungsten carbide. Titanium silicide was found to be a very good conductor of heat and electricity, a point which might be of importance in some applications, as, for instance, in the production of sintered cutting tools or drills where heat, created by friction, should be quickly removed from the cutting edge.

Other Titanium Compounds

The same procedure can be used for the production of other titanium compounds such as titanium boride, and with small modifications, titanium nitride. The use of a metallic hydride, as illustrated by the above example, has the following advantage in the preparation of various compounds. It creates its own atmosphere of 100 per cent pure hydrogen which by other means is extremely difficult to obtain. It eliminates all the waste of materials and gives a product of the exact composition and in a form which could be easily used in the subsequent preparation of grinding wheels, sintered cutting tools, drills, etc.

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[4] *Compt. rend.*, Vol. 110, 1890, p. 1368.
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[6] *Compt. rend.*, Vol. 143, 1906, p. 224.

(Concluded from page 178)

The Alloy Steel Casting Output

Last year, in the compilation of data for an article on "Trends in the American Alloy Steel Industry," published in METALS AND ALLOYS, July, 1937, page 191, it was possible to publish fairly reliable estimates of the alloy steel casting production, based on data furnished by the S. F. S. A. For example in 1934, 1935 and 1936, the percentage of alloy castings of the total was estimated by that society at about 14.5, 15.5 and 16.5 per cent respectively. For 1937 such an estimate is not available. It is believed, however, from reliable sources, that the percentage last year was no more than 15.5 per cent, due to the increased tonnage of carbon steel castings produced. Based on the foregoing estimates and statements, there has been added to Table II, as it originally appeared, the estimated production of alloy steel castings.

From the statistics of Table II it is evident that the steel casting output of at least 1,027,800 gross tons in 1937, based on the data of the S. F. S. A., is the largest since 1930 when it was 1,104,215 tons.

Some Additional Data

It is possible to present some interesting estimated data on the production in the United States of all types of castings for 1936 and 1937. Taking the figures of the S. F. S. A. as a basis and estimating the stainless and manganese steel castings output, the following table is compiled in net tons:

	1936	1937
Misc. and Special Comm.	755,8 0	955,400
For Companies' Own Use	154,200	195,700
Manganese	50,000	65,000
Stainless or High Alloy	5,000	7,500
	965,000	1,223,600
In gross tons	861,000	1,092,675

Figured to gross tons the 1937 estimated total of 1,223,600 net tons is approximately 1,092,675 gross tons, which compares with the 1,027,800 gross tons in Table II. The discrepancy is probably explained by the fact that manganese and heat and corrosion resisting alloy castings are not included in the statistics of the S. F. S. A.

The data presented in the foregoing are interesting not for their accuracy, but as at least showing the production trend of the American steel foundry industry.

Letters to the Editor

Metallographic Examination of Sheet and Strip

To the Editor: Ordinarily metallographic examination of sheet and strip is executed by holding a number of pieces of the material between securely tightened polishing clamps. Often grinding media or etching reagents get between the members of this compressed pack and cause considerable trouble due to scratches or strains on the polished surface. The net result in this case is not only a spoiled specimen, but, very likely, increased blood pressure for the metallographer also.

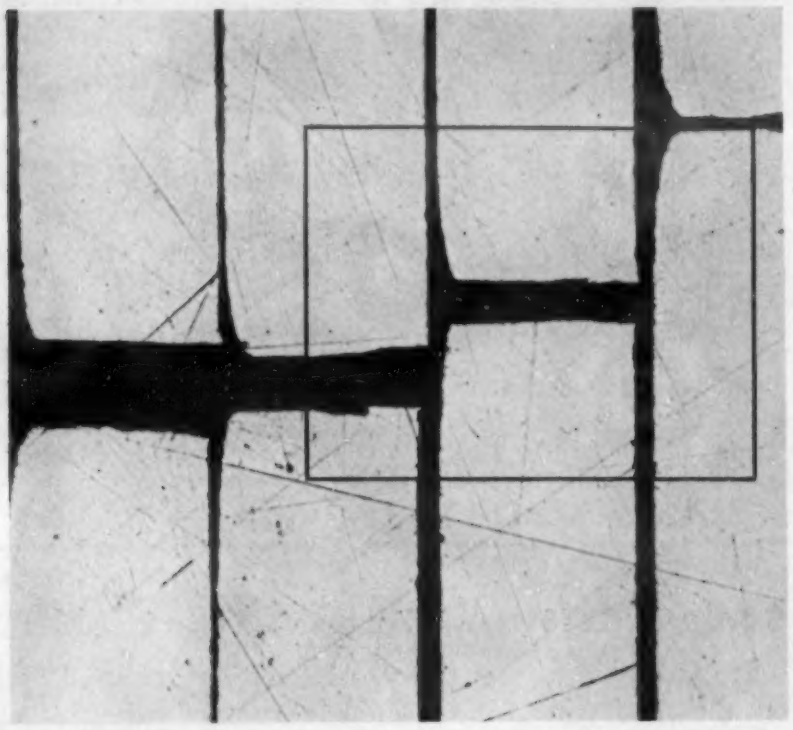

Fig. 1

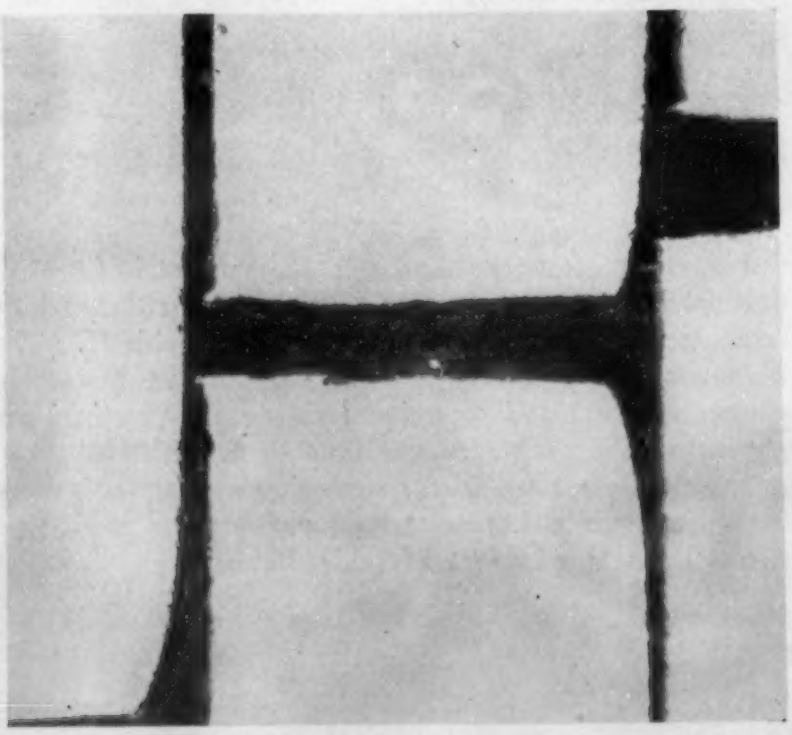

Fig. 2

A short time ago the writer had occasion to study the microstructures of some very thin strip, 0.004 in. thick. It was decided to try a new wrinkle in the method of mounting this strip. This involved coating each piece of strip with "Tornesite" (a synthetic rubber dissolved in a volatile organic solvent). The specimens were then mounted in the polishing clamps, and the excess tornesite squeezed out by compressing the pack. The mounted specimens were allowed to dry over night, and then polished and etched.

The results were very satisfactory. The tornesite completely filled the interstices due to the slight irregularities in the surface of the strip. The tornesite withstood the polishing and etching very well. No trouble was encountered from grinding media or etching reagents getting between the members of the pack.

The accompanying photomicrographs show the following:

Fig. 1—Tornesite between strip specimens as polished with levigated alumina. 200X.

Fig. 2—Tornesite between strip specimens as polished with magnesia. 400X. Fig. 2 is an enlarged view of part of Fig 1 as indicated by the blocked-out area.

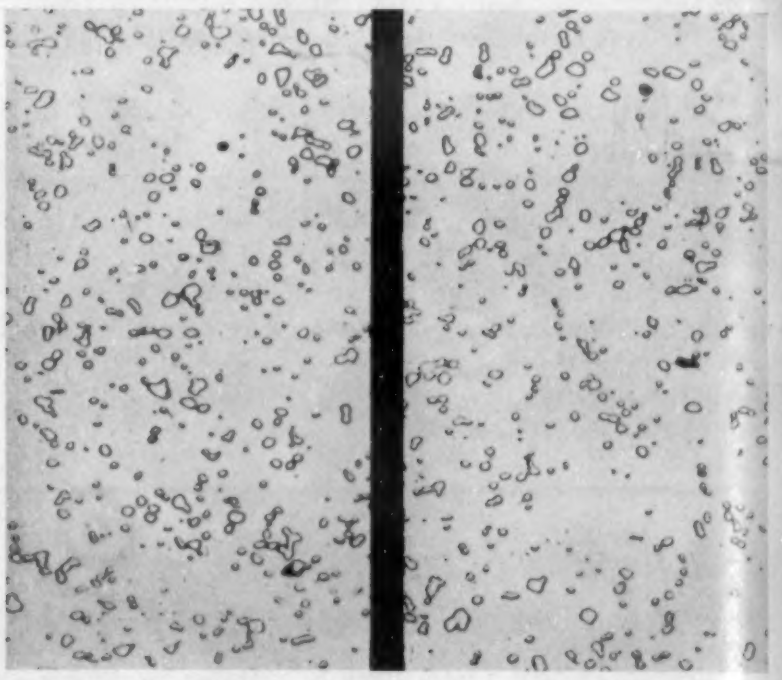

Fig. 3

Fig. 3—Two adjacent strips, etched to show spheroidized cementite. Note clear focus at specimen edges. 1000X.

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Sulphide Inclusions in Iron and Steel

To the Editor: Before being sure that the inclusions illustrated by Dr. Tesche on page 78 of the March issue of METALS AND ALLOYS is really a section of a hexagonal crystal, some evidence should be offered that the hexagonal section is not through the cube center at right angles to the cube diagonal. [We learn now that Dr. Tesche spells his name with a "T" and not a "J."]

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To the Editor: In my contribution to METALS AND ALLOYS in the March issue, 1938, page 78, a regrettable oversight caused me to give too high a figure for the seemingly possible FeS-content of the inclusion shown. Assuming the solidus temperature of 1490 deg. C. for the steel in question, one must of course use the intersection of this temperature with the solidus line in the FeS-MnS diagram to find the maximum possible content of FeS. Taking the (rather vague) solidus-line in Röhl and Oberhoffer's diagram (see E. Houdremont, "Einführung in die Sonderstahlkunde," Springer, 1935, p. 529) one would find a maximum FeS content of only about 13 per cent.

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